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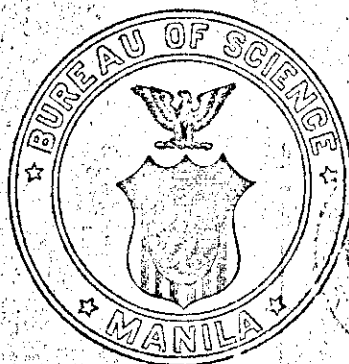
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THE PHILIPPINE JOURNAL OF SCIENCE

A. CHEMICAL AND GEOLOGICAL SCIENCES
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THE STRIPPING AND THE ANALYSIS OF GALVANIZED IRON¹

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INTRODUCTION

The extensive use of galvanized-iron products has led to the development of a voluminous bibliography on the manufacture, corrosion, testing, and stripping of zinc-coated iron. With the present increase in the price of zinc, from 10.10 pesos² per hundred pounds (about 45.36 kilograms) in July, 1914, to 37.50 pesos in January, 1916, the recovery of that metal becomes a problem of more and more importance.³ It is the purpose of this paper to give a brief outline of various methods of analysis and stripping heretofore proposed, together with the results obtained in this laboratory.

When a shipment of galvanized-iron roofing is to be analyzed, so large a number of determinations is often necessary that a laboratory test should be extremely simple and rapid, as well as accurate. Although there are many factors, such as the purity and porosity of the zinc, influencing the durability of galvanized iron, in general, the most important factor is the thickness of the coating.⁴ The amount of iron and other impurities in the zinc is generally small, and no serious error is involved even if they are included as part of the weight of

¹ Received for publication March 25, 1916. ✓

² One peso Philippine currency equals 50 cents United States currency.

³ Juretzka, F., *Metall u. Erz* (1915), 3, 63 and 94. ✓

⁴ Walker, W. H., *Proc. Am. Soc. Test. Materials* (1909), 9, 431. ✓

the coating, especially since the lack of uniformity in galvanized plate and the difficulty often encountered in getting sample pieces cut to exactly the same size make very concordant results out of the question. Therefore the determination of the amount of zinc and zinc-iron alloy per unit area is often relied upon for practical tests. Many quick methods have been developed to determine this factor. With these methods the zinc is removed by immersing the plated iron in a solution of the salt of some metal which will be replaced in solution by zinc, but not by iron, or else advantage is taken of the difference in solubility of zinc and iron in acids and alkalies.

The Preece test⁵ employs a solution of copper sulphate into which a measured piece of zinc plate is dipped. Copper forms a spongy black deposit on zinc and a bright, hard deposit on iron; the number of one-minute immersions necessary to remove the zinc, shown by the first appearance of a bright red copper deposit, serves as a basis for calculating the thickness of the coating. The limitations of this method have been thoroughly discussed elsewhere.⁶ Patrick and Walker⁷ have suggested the use of basic lead acetate to replace the copper sulphate of the Preece test;⁸ in this case zinc is dissolved and spongy lead is precipitated, while the iron remains unattacked.

Both acids and alkalies can be used to remove zinc from iron without appreciable attack on the latter. In this case, owing to the difference in potential of the two metals, the zinc in contact with the iron inhibits the solution of the latter, while the rapidity with which the former dissolves is increased. A simple method consists in dissolving the zinc from the iron by immersion in sulphuric acid,⁹ determining the amount of iron in solution, and adding it to the weight of the remaining plate. The weight of the coating per unit area is calculated from the difference between the weight of iron and the original weight of plate. For certain concentrations of (dilute) sulphuric acid¹⁰

⁵ Walker, loc. cit. ✓

⁶ Walker, loc. cit.; Patrick, W. A., and Walker, W. H., *Journ. Ind. & Eng. Chem.* (1911), 3, 238.

⁷ Loc. cit.

⁸ It is interesting to note that had an ammoniacal, instead of a neutral, solution of copper sulphate been used, the Preece test would have lost many of its limitations. Although perhaps not quite so convenient as the lead acetate method, the use of ammoniacal copper sulphate solution (see experiment 25) gives reliable and concordant results.

⁹ Burgess, C. F., *Electrochem. & Met. Eng.* (1905), 3, 19; Dudley, C. B., *Trans. Am. Soc. Test. Materials* (1909), 9, 441.

¹⁰ Burgess, loc. cit., recommends the use of $\frac{1}{3}$ N sulphuric acid.

the attack on the iron of the base is so slight that it may be disregarded. Bauer¹¹ takes advantage of the frequently recorded¹² inhibitive effect of arsenic on the dissolution of iron in sulphuric acid to recommend the addition of arsenious acid to dilute (2 per cent) sulphuric acid in making the separation.

Hydrochloric acid is capable of similar utilization. The following analytical data (Tables II and V) show that concentrated hydrochloric acid can be used for stripping without appreciable effect on the iron of galvanized sheet, while Witt¹³ recommends the use of dilute hydrochloric acid. Aupperle¹⁴ suggests the use of concentrated hydrochloric acid (specific gravity, 1.2) with an addition agent, antimony trichloride (SbCl_3), to protect the iron. In this case the action is probably similar to the inhibiting effect of arsenious acid on the action of sulphuric acid.¹⁵

Alkalies also can be used. Walker¹⁶ reports that the zinc of galvanized iron, exclusive of the zinc-iron alloy, may be removed quantitatively by dissolving in a hot caustic soda solution. The use of hot sodium peroxide solution is recommended by Meyer.¹⁷

There are several other stripping solutions mentioned¹⁸ in the literature, although most of these do not yield sufficiently accurate results to serve in analytical methods, or have not been developed for analytical purposes.

EXPERIMENTAL PART

The first method to be tested in the present series of experiments was that of Meyer.¹⁹ Briefly stated, this method con-

¹¹ Bauer, O., *Mitt. kgl. Materialprüfungsamt* (1914), 32, 448.

¹² Millon, E., *Compt. rend. Acad. Sci.* (1845), 21, 37; Burgess, C. F., *Trans. Am. Electrochem. Soc.* (1905), 8, 165; (1906), 9, 199. For a possible explanation for this phenomenon see Watts, O. P., *ibid.* (1912), 21, 337.

¹³ Witt, J. C., *This Journal, Sec. A* (1916), 11, 154.

¹⁴ Aupperle, J. A., *Metal. Ind.* (1915), 13, 329; *Iron Age* (1915), 96, 132.

¹⁵ Beneker, U. S. Patent 914,916 (March, 1909), uses dilute hydrochloric acid containing from 0.001 to 0.005 per cent arsenic as a cleaning or pickling bath for iron or steel.

¹⁶ Loc. cit.

¹⁷ Meyer, K., *Zeitschr. f. angew. Chem.* (1909), 22, 68; Serger, H., *Zeitschr. f. Untersuch. d. Nahrungs- u. Genussmittel* (1913), 25, 465.

¹⁸ Broemme, E., and Steinau, R., U. S. Patent 1,042,315 (October, 1912). The use of alkali or alkaline earth bisulphates or bisulphites; the use of zinc chloride in slightly basic water solution; Weber, U. S. Patent 1,122,272 (December, 1914).

¹⁹ Loc. cit.

sists in boiling weighed pieces of galvanized iron with sodium peroxide and water and determining the loss in weight. Typical analyses follow:

TABLE I.—Analyses of galvanized iron by the Meyer method.

Sample.*		Loss after treatment No.—		Coating in sample. ^b	Weight of coating. ^b	
No.	Weight.	I.	II.		Per square foot.	Per square decimeter.
	Grams.	Grams.	Grams.	Per cent.	Ounces.	Grams.
1	14.430	0.877	1.526	10.52	1.94	5.92
2	14.912	0.842	1.556	10.42	1.97	6.03
3	14.483	1.531	1.543	10.35	1.95	5.98
4	14.327	1.507	1.530	10.64	1.94	5.95

* Each sample was 5.08 by 5.08 centimeters (2 by 2 inches).

^b Computed from loss of weight after second treatment.

The Meyer method gives concordant and reliable results. However, it was devised especially for the stripping of tin plate and is better adapted to that process than to the stripping of galvanized iron because of the relatively large amounts of zinc used for coating iron. Treatment with sodium peroxide must be repeated several times to insure the complete removal of the zinc coating from ordinary galvanized iron, so that the process becomes tedious.

Some of the experiments performed in the course of this study have little analytical or commercial value at present, but yield interesting information regarding the potentials of metals in various solution. We have divided them into two classes—namely, those in which the zinc has been dissolved by immersion in the stripping solution and those in which electric current has been used to aid or control the action.

Table II gives examples of stripping baths of the first class. For the tests enumerated, pieces were cut from a sheet of galvanized iron, which analysis had shown to be fairly uniform in composition. Therefore the results obtained may be considered comparable. As galvanized iron at best is of varying composition, differences of less than 0.1 per cent have little significance. A few tests by standard methods (Nos. 5, 16, etc.) are inserted for comparison.

TABLE II.—Removal of zinc from galvanized iron by immersion.

Experiment No.	Solution used.	Weight of sample.	Loss on immersion.			Remarks.
			Grams.	Grams.	P. ct.	
5	Sodium peroxide (Meyer method).	8.494	0.830	9.77		
6	Nitric acid (concentrated).....					Rapid and complete dissolution.
7	Hydrochloric acid (sp. gr. 1.2)....	5.773	0.551	9.55		Loss after 30 minutes additional, 0.001 gram.
8	Hydrochloric acid (25 per cent by volume).	5.094	0.495	9.73		
9	Sulphuric acid (50 per cent by volume).					Action is very slow, but iron is attacked.
10	Sulphuric acid (25 per cent by volume).	4.957	0.497	10.02		Action continues indefinitely.
11	Sulphuric acid (5 per cent by volume).	5.348	0.505	9.44		Loss after 80 minutes additional, 0.002 gram.
12	Sodium bisulphate (concentrated).	4.413	0.417	9.45		Loss after 18 hours additional, 0.002 gram.
13	Phosphoric acid (25 per cent by volume).	5.182	0.496	9.57		Loss after 60 minutes additional, nil.
14	Phosphoric acid (2 per cent by volume).	4.228	0.400	9.45		
15	Acetic acid (25 per cent by volume).	5.822	0.560	9.61		Required 24 hours for completion. Loss after 5.5 hours additional, 0.0025 gram.
16	Lead acetate	5.123	0.496	9.68		Loss after 90 minutes additional, 0.0015 gram.
17	Lead acetate plus sodium hydroxide.	5.027	0.468	9.30		Loss after 20 hours additional, 0.0015 gram.
18	Lead acetate plus acetic acid	4.705	0.428	9.09		Loss after 90 minutes additional, 0.0005 gram.
19	Lead nitrate	4.435	0.303	6.83		Deposit is hard and adherent.
20	Lead nitrate plus nitric acid.....	4.653	0.428	9.19		Action is slow.
21	Lead nitrate plus sodium hydroxide.	4.257	0.402	9.44		Deposit is not readily removed. Loss after 18 hours additional, 0.0035 gram.
22	Lead chromate plus sodium hydroxide.					No action.
23	Cadmium nitrate					Do.
24	Cadmium nitrate plus ammonium hydroxide.	4.159	0.398	9.57		Action is very slow; coating is hard to remove.
25	Copper sulphate plus ammonium hydroxide.	4.063	0.894	9.70		Action is very slow.
26	Copper sulphate plus tartaric acid plus potassium hydroxide.	3.953	0.381	9.64		Copper scale is readily removed by scrubbing.
27	Cobalt acetate	4.553	0.293	6.43		Reaction not completed at end of 10 days.
28	Cobalt acetate plus ammonium hydroxide.	2.669	0.255	9.56		Action proceeds with effervescence.
29	Chromium nitrate	4.549	0.467	10.36		72 hours required for completion, coating is hard and adherent, and iron is attacked.

* The iron base is attacked on continued immersion.

TABLE II.—*Removal of zinc from galvanized iron by immersion—Continued.*

Experiment No.	Solution used.	Weight of sample.	Loss on immersion.		Remarks.
		Grams.	Grams.	P. ct.	
30	Chromium nitrate plus sodium hydroxide.	3.684	0.356	9.68	72 hours required for completion; coating is hard and adherent.
31	Aluminium nitrate.....	4.629	0.458	9.89	
32	Aluminium nitrate plus sodium hydroxide.	4.259	0.068	1.61	Reaction not completed at end of 10 days.

The results in Table II, for the most part, are self-explanatory, yet some of them merit further attention.

Theoretically the removal of zinc from iron is easy, since the potential of the former is the higher in most solutions. In stripping with the metallic salts, it would seem necessary merely to find the salt of a metal whose potential, in any given solution, is lower than that of zinc and higher than that of iron. Practically, however, the manner in which the potentials of metals fluctuate in different solutions, the character of the metallic deposits formed, and other factors make the operation less simple.

Iron, cathodic to zinc in most acids, does not assume the passive state in contact with zinc; hence galvanized iron is completely destroyed in concentrated nitric acid (No. 6).²⁰

The action of lead salts is interesting and peculiar. The precipitated lead from lead acetate in acid solution (No. 18) or in approximately neutral solution (No. 16) is crystalline in appearance, while that from a solution made alkaline with sodium hydroxide (sufficient to dissolve the precipitate formed) (No. 17) is velvety. The deposits obtained from lead nitrate solution (No. 19) are crystalline, but much harder to remove than those from lead acetate solution. The acidified solution of lead acetate (No. 18) did not attack plate so well as a nearly neutral solution (No. 16). A further peculiarity is the fact that a lead acetate or lead nitrate solution to which sodium hydroxide has been added (lead hydroxide) in sufficient quantity to redissolve the precipitate formed (sodium plumbite) will

²⁰ However, the tin of tin plate can be completely removed by concentrated nitric acid, without affecting the iron base, although according to de la Rive [Gore, *The electrolytic separation of metals*. Van Nostrand & Co., New York (1894), 56], tin is electropositive to both zinc and iron in concentrated nitric acid.

strip zinc, whereas lead chromate dissolved in sodium hydroxide leaves galvanized iron unattacked.

Copper salts, which generally attack both zinc and iron, may have selective action in alkaline solution (Nos. 25 and 26). Ammoniacal and alkaline solutions of salts of other metals, such as aluminium (Nos. 31 and 32), cadmium (Nos. 23 and 24), cobalt (Nos. 27 and 28), and chromium (Nos. 29 and 30), have selective action, although the salts themselves have little or no such effect.

Of the cases mentioned, the precipitation of such metals as chromium, copper, lead, and aluminium from alkaline solution is of special interest because of the uncertain position of the metals in the complexes formed when their salts are dissolved in alkalis.

The fact that iron is generally attacked very little when it is used as anode in alkaline or oxidizing solutions has long been made the basis of methods of separation of metallic coatings from iron.²¹ The separation is sufficiently complete and clean cut to serve as a rapid and accurate method of analysis of galvanized iron, as the results in Table III show. In the experiments here recorded, no particular effort was made to regulate the current. A voltage of about 3 and a current density of approximately 15 to 25 amperes per square decimeter were maintained, the stripping being completed in a few minutes. The galvanized iron was cut from the sheet used in the tests enumerated in Table II.

TABLE. III.—*Stripping of zinc from iron with the aid of an electric current.*

Experiment No.	Bath.	Sample.		
		Weight.	Loss.	
			Grams.	Per cent.
23	Potassium chlorate, saturated solution.....	1.996	0.189	9.49
34	Potassium nitrate, saturated solution.....	2.766	0.264	9.54
35	Potassium nitrate, saturated solution.....	2.300	0.217	9.43
36	Potassium nitrate, saturated solution.....	2.229	0.213	9.53
37	Sodium nitrate, 30 per cent solution.....	4.055	0.393	9.69
38	Chromium nitrate, 20 per cent solution.....	2.601	0.274	10.53
39	Chromium nitrate, 20 per cent solution.....	2.455	0.263	10.72
40	Potassium hydroxide, 20 per cent solution.....	3.918	0.380	9.70
41	Sodium hydroxide, 20 per cent solution.....	4.454	0.422	9.47

Chromium nitrate allowed a slight although appreciable dissolution of the iron base. With the possible exception of the case of

²¹ Burgess, C. F., *Trans. Am. Electrochem. Soc.* (1903), 4, 31.

chromium nitrate, there was no noticeable attack on the iron base on continued passage of current.

The results of the foregoing experiments indicate that many of the methods enumerated are capable of being used for quantitative analyses; hence some of the more promising were studied in greater detail. For these experiments samples of the same galvanized iron (different from that used in the foregoing tests), cut with shears as accurately as possible into square of desired size, were used.

The results recorded in Table IV were obtained by making galvanized iron the anode in 30 per cent sodium nitrate solution.

TABLE IV.—*Stripping of galvanized iron with an electric current. Galvanized sheet anode, platinum cathode. Bath, 30 per cent sodium nitrate (NaNO_3) solution, except as noted; current, 0.7 to 1.0 ampere; voltage, 3 to 5; size of plate, 3.8 by 3.8 centimeters (1.5 by 1.5 inches), except as noted.*

Experiment No.	Sample.	Loss.			Weight of coating.	
					Per square foot.	Per square decimeter.
	Grams.	Grams.	Per cent.	Ounces.	Grams.	
42	8.232	1.203	14.61	2.73	8.33	
43	7.948	1.201	15.10	2.72	8.31	
44	8.345	1.217	14.93	2.76	8.43	
45	8.113	1.186	14.26	2.69	8.21	
46	33.175	4.650	14.02	2.64	8.07	
47	8.068	1.127	13.97			

* This sample was 7.6 by 7.6 centimeters (3 by 3 inches).

^b In a bath of 20 per cent sodium hydroxide

Only a few minutes were necessary completely to remove the zinc from the iron. There was no residual zinc on the stripped plate. The results obtained show as good agreement as could be expected, considering the lack of uniformity of zinc coatings, the size of the samples used for analysis, and the errors incident to cutting out squares with ordinary tin shears.

The presence of iron could always be shown in the solution after stripping had been accomplished. That this was not due to an appreciable extent to attack on the iron base is shown not only by the constancy of the results recorded for the thickness of the coating, but also by the constancy of the amount of iron removed in the different trials. Duplicate determinations fixed the amounts of iron from pieces of galvanized iron 3.8 by 3.8 centimeters (1.5 by 1.5 inches) as 0.046 and 0.048 gram,

respectively. These figures are equivalent to losses of iron of 0.319 and 0.332 gram per square decimeter (0.105 and 0.109 ounce per square foot), with which the loss (0.11 ounce per square foot) recorded by Witt²² for the same sample of galvanized iron when stripped with hydrochloric acid is in good agreement. There is always a layer of zinc-iron alloy formed when iron is galvanized by the "hot process," whereas little²³ or no²⁴ such layer is formed when iron is electroplated. Therefore it is evident that the iron found in the stripping bath was largely due to the zinc-iron alloy formed in the process of hot galvanizing.

As has been shown (Table II), sulphuric acid alone can be used for the analysis of galvanized iron with reliable results, provided the acid is used in proper dilution. However, acid strong enough to attack galvanized iron may be used successfully if electric current is used and the plate to be stripped is made the cathode.²⁵ That the iron is protected from attack by this method is shown by the data in Table V.

TABLE V.—Stripping of galvanized iron with electric current; plate as cathode. Size of plate, 3.8 by 3.8 centimeters (1.5 by 1.5 inches), except as noted; bath, sulphuric acid; current, 0.75 to 1.5 amperes; voltage, 3.

Experiment No.	Strength of acid by volume.	Sample.	Loss.		Weight of coating.	
					Per square foot.	Per square decimeter.
	Per cent.	Grams.	Grams.	Per cent.	Ounces.	Grams.
48	a 2	7.979	1.081	13.55	2.44	7.45
49	b 50					
50	20	8.285	1.155	13.94	2.61	7.96
51	20	8.230	1.135	13.79	2.56	7.82
52	20	c 16.387	2.372	14.48	2.67	8.17

^a Action is very slow, especially on side nearest anode.

^b No appreciable action in thirty minutes.

^c This plate was 3.8 by 7.6 centimeters (1.5 by 3 inches).

Analysis showed that iron was also dissolved in this process. The maximum amount determined in the solution was 0.047 gram. The agreement with our own previously recorded values

²² Loc. cit.

²³ Walker, W. H., *Journ. Ind. & Eng. Chem.* (1912), 4, 397.

²⁴ Bauer, loc. cit.

²⁵ Reed, C. J., *Trans. Am. Electrochem. Soc.* (1907), 11, 181, recommends the removal of mill scale from iron by making the iron the cathode in sulphuric acid.

(Table IV) for the same galvanized iron shows clearly that this iron was part of the zinc-iron alloy, not part of the iron base. However, as might be expected, the rate of solution of zinc is somewhat retarded by this process. The separation is completed in a very few minutes, and the iron base, so far as could be determined, is protected.

Finally a series of determinations was made, using different acids of varying concentrations. The results, which are self-explanatory, are given in Table VI.

TABLE VI.—*Stripping of galvanized iron with acids. Temperature, 30° C. Size of samples, 3.8 by 3.8 centimeters (1.5 by 1.5 inches).*

Experiment No.	Bath.	Sample.	Loss.				Weight of coating.	
							Per square foot.	Per square decimeter.
		Grams.	Grams.	Per cent.		Ounces.		Grams.
53	Sulphuric acid, 2 per cent, plus arsenic trioxide.....	8.128	1.015	12.48		2.30		7.03
54	Phosphoric acid, 25 per cent by volume.....	8.336	a 1.122	13.49		2.55		7.77
55	do.....	8.102	a 1.128	13.92		2.56		7.81
56	Hydrochloric acid (sp. gr., 1.19)	7.941	b 1.099	13.84		2.49		7.61

^a No additional loss after reimmersion for one hour.

^b Loss <0.002 gram after thirty minutes additional immersion.

In each case the removal of zinc is characterized by effervescence, which ceases entirely when the iron of the base is reached. Phosphoric acid reacts slowly, but the stripped iron can be left immersed for a long time without appreciable loss.

DISCUSSION

The experiments here enumerated,²⁶ aside from their possible application to analytical or commercial problems, are of interest in their bearing on the question of the potentials of metals in different baths and the replacement of a metal from its salts by another metal. That the replacement series of the metals differs not only in solutions of different substances in a given solvent, but also in solutions of the same substance in a constant solvent with factors such as change of temperature, pressure, concentration, magnetic influence, and the like is well known.²⁷

²⁶ The applicability of some of the methods enumerated above to the removal of tin from tin plate will be discussed in another paper.

²⁷ Cf. Gore, G., loc. cit.; idem, *Proc. Roy. Soc.* (1879), 30, 38; Christy, S. B., *Trans. Am. Inst. Min. Eng.* (1900), 30, 864.

A variation of the solvent²⁸ makes the subject still more complicated.

In this brief series of experiments there are several "reversals" of potential. Thus copper sulphate attacks both zinc and iron in aqueous solution, as might be expected from its position in the "electrochemical series," but on the addition of ammonia to solutions of certain copper salts, the copper apparently occupies a place above iron and below zinc. The same holds true for an alkaline copper sulphate solution (No. 26). Zinc replaces aluminium²⁹ (Nos. 31 and 32) from aluminium nitrate solution. The last reaction is retarded by the addition of sodium hydroxide.

Tzentnerschwer and Druckker³⁰ found that zinc reacts with solutions of cobalt chloride and cobalt sulphate, but only with very concentrated cobalt nitrate solutions. This is interesting in view of our experiments 26 and 27 with cobalt acetate. We have found that an ammoniacal solution of cobalt nitrate (like ammoniacal cobalt acetate No. 27) reacts very quickly with galvanized plate and gives a quantitative separation of zinc from iron.

The variation in the single potentials of zinc in different aqueous solutions has been studied in detail by Patten and Mott,³¹ who found a difference of over 1 volt between the highest (+ 1.0 volt in KOH + KCN) and the lowest (— 0.08 volt in KMnO_4 + K_2CrO_4) values obtained. Other metals doubtless show equally great variations. Perhaps the fact that the potential of zinc is lowered in oxidizing solutions such as nitrate, chromate, or permanganate of potassium accounts for the failure of a solution of lead chromate in sodium hydroxide to attack galvanized iron.

SUMMARY AND CONCLUSIONS

Various methods of analyzing galvanized iron, or of stripping zinc from iron, have been studied and developed.

The separation of zinc from iron with phosphoric acid, sodium bisulphate, hydrochloric acid, or sulphuric acid is sufficiently rapid and complete to serve as a quantitative analytical

²⁸ Gates, C. B., *Journ. Phys. Chem.* (1911), 15, 97; Ghosh, J. C., *ibid.* (1915), 19, 720.

²⁹ Preliminary experiments in this laboratory indicate that the potential of zinc is several tenths of a volt above that of aluminium in a normal sodium nitrate solution.

³⁰ Tzentnerschwer, M., and Druckker, Y., *Journ. Russ. Phys. Chem. Soc.* (1915), 47, 528.

³¹ Patten, H. E., and Mott, W. R., *Trans. Am. Electrochem. Soc.* (1903), 3, 317.

method. Acetic acid gives accurate results, but the action is slow.

The separation can also be effected by the use of metallic salts, notably certain salts of lead, cadmium, copper, cobalt, chromium, and aluminium. The experiments with metallic salts give an indication of the changes in the potential of metals which occur in different liquids.

Stripping and analysis may be accomplished with the aid of the electric current, by making galvanized iron the cathode in sulphuric acid, or by making it the anode in concentrated caustic alkali solutions or in oxidizing solutions like sodium nitrate.

In the methods enumerated, the iron removed from the galvanized plate is largely that contained in the zinc-iron alloy present in the coating and is not due to corrosion of the iron base.

THE TESTING OF GALVANIZED IRON ¹

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TWO TEXT FIGURES

INTRODUCTION

There are four general methods for galvanizing ²—namely, hot galvanizing, electrogalvanizing, sherardizing, and cowperizing. The essentials of each are briefly as follows:

Hot galvanizing.—This process was patented by Crawfurd ³ in 1837. The iron is first cleaned in dilute hydrochloric or sulphuric acid, washed in water, and then passed into a bath of molten zinc. The temperature is usually kept as low as possible to avoid too much volatilization of the zinc and too great a loss from alloying with the iron. Excess zinc is removed either by passing between rollers or by shaking or centrifuging. The process is economical in time, but wasteful in zinc. According to Turnbull ⁴ the distribution of zinc in a hot galvanizing bath is as follows:

	Per cent.
Coating on the articles	68
Dross	18
"Ashes"	12
Volatilized	2

Electrogalvanizing.—After being thoroughly cleaned, the iron is placed in a solution of a zinc salt and the zinc is deposited by electrolysis. The anode is usually lead or zinc. This process is extensively used for small objects, such as bolts and nails, and also for boiler tubes.

Sherardizing.—In this method the iron is cleaned and placed in a large iron drum which contains zinc dust. The drum is then heated to a temperature of from 260° to 315°C. The container should be air-tight, and most of the air should be removed

¹ Received for publication November 24, 1915.

² See Sherard Cowper-Coles, *Electrochem. & Met. Ind.* (1908), 6, 189.

³ Thorp's Dictionary of Applied Chemistry. Longmans, Green, & Co., London (1913), 5, 810.

⁴ *Journ. Inst. Metals* (1914), 12, 301.

to prevent much of the zinc from oxidizing. The thickness of the coating depends on the time and the temperature.

Cowperizing.—The iron is placed in a drum made of wire netting and is treated with zinc vapor in an atmosphere of hydrogen. The reducing action of the hydrogen aids in keeping the zinc free from oxide and thus insures a good adhesion of the deposit. This process is especially suitable for coating articles which have threads or which require to be accurately fitted, because the zinc is evenly distributed.

Only the hot galvanizing and the electrogalvanizing processes are used in the manufacture of galvanized sheets. The present work has been done with sheets galvanized by the former method.

The question of galvanized sheets is of importance in the Philippine Islands. They are extensively used as a roofing material to replace nipa. They are light and, of course, not inflammable. About 80 to 90 per cent come from the United States and are bought under the specifications that for each 900 square centimeters there must be a minimum of 54.9 grams of coating (two ounces per square foot).⁵ It seemed advisable to investigate various methods of determining the amount of the coating and to decide if possible which is the best with reference to accuracy and the time, labor, expense, and other factors of applying it.

In this connection the structure of galvanized iron is of interest. There is no sharp line of demarcation between the iron base and the zinc coating, but between the two is a series of zinc-iron alloys. The alloys nearest the iron base contain mostly iron. From this outward there are other alloys, each with a lower percentage of iron, till the zinc itself is reached. Warren⁶ expresses the relationship very clearly when he says: "Zinc in galvanized iron exists in two states. (1) Part of the zinc forms an alloy with the iron (2) zinc adheres to this alloy mechanically."

Arthur and Walker⁷ have made a study of the structure of galvanized iron by microscopic methods. They state that the

⁵ In the United States, tests on galvanized iron are reported in terms of ounces of zinc per square foot. In order that this paper may be easily compared with others on the subject, results are given in both systems of weights and areas.

⁶ *Phil. Mag.* (1871), IV, 41, 132.

⁷ *Journ. Ind. & Eng. Chem.* (1912), 4, 397; see also v. Vagesack, *Zeitschr. f. anorg. Chem.* (1907), 52, 30.

binding alloy is present even in iron that has been electrogalvanized or sherardized. In hot galvanized iron, crystals of FeZn_3 and FeZn_7 have been found.

VARIOUS METHODS OF TESTING

A number of methods have been published for determining the amount of zinc coating on galvanized objects. Among them may be mentioned the amalgamation method and the use of solutions of copper sulphate, sodium hydroxide, lead acetate, etc. The various tests may be divided into two groups:

1. The galvanized object is placed in a solution which will attack the zinc, but has little effect on the iron base. After a given period of time it is removed, cleaned of any loosely adhering substances, and again placed in the solution. The strength of the solution is known, and the temperature is kept within certain limits. When all the zinc is removed at any point, the test is regarded as complete, and the number of immersions are recorded.

2. All the zinc is removed. The weight per unit area or unit length is calculated.

A test of the second group is to be recommended whenever practicable. Such a test is now almost universally used for galvanized sheets and is well adapted to wire. Tests of the first group are usually applied to all irregular objects such as bolts and nuts. Specifications are written on that basis, and considerable work would be required to determine just how much coating should be found on all the various articles that are now galvanized and to rewrite the specifications. However, it seems likely that this will be done in time and that all tests of the first group will go out of use.

The amalgamation, or mercury, method seems to have been one of the earliest used. Warren^{*} found that by putting a clean galvanized object into mercury all the free zinc was removed. The zinc, which was alloyed with iron, combined with mercury, also, in the ratio of 7:11. This new alloy could then be volatilized in a nonoxydizing flame and the zinc calculated and added to that previously removed. Of course, this procedure would not be satisfactory for routine work.

Sodium hydroxide solution is sometimes used for removing the zinc from galvanized iron. This method is not satisfactory because it is slow and because some of the zinc-iron alloys are not attacked.

^{*} Loc. cit.

The copper sulphate, or Preece, test is the one still in most general use for all galvanized articles except sheets. An outline of the method is as follows:

A strong solution of copper sulphate is shaken with copper oxide to neutralize any acid present and is then diluted to density 1.186 at 18.5°C. A galvanized article is placed in this solution for one minute and is then removed and cleaned. This operation is then repeated until a bright deposit of copper is formed on the iron base. In order to pass specifications, an object must withstand a given number of immersions. Many criticisms may be offered to this method as pointed out by Walker⁹ and by Patrick and Walker,¹⁰ who have studied it in detail. They state that since the zinc coating is not homogeneous and the zinc-iron alloys are less electropositive to the iron than is the zinc, the zinc does not go into solution at a constant rate of speed:

Since the rapidity with which the zinc or zinc alloy will pass into solution, and an equivalent weight of copper be precipitated in its place, is a function of the difference of potential between the two metals, it will be seen that the rate of solution must of necessity change as we pass from the zinc to the alloy. The coating in the so-called sherardized iron and some kinds of electro-galvanized iron consists so largely of an iron-zinc alloy that any test or measurement based upon an assumed uniformity in rate of solution is liable to grave error and untrustworthy.

THE LEAD ACETATE METHOD

Patrick and Walker¹¹ devised the lead acetate method as a substitute for the Preece test. They recommended that it be used to determine the weight of zinc coating per unit length or area, but stated also that, even if it is used in the same way as the Preece test, it is more satisfactory. A solution is made by dissolving 400 grams of crystallized lead acetate in one liter of water. To this are added 4 grams of litharge to neutralize any acid present and to give the solution a slightly basic reaction. After filtering, the solution is ready for use. A piece of wire 7.6 to 15.2 centimeters (3 to 6 inches) long or a galvanized plate 5.08 by 5.08 centimeters (2 by 2 inches) is weighed and placed in a quantity of the solution for three minutes. The zinc goes into solution and a deposit of metallic lead forms on the plate or wire. The object is taken from the liquid, and the lead is removed. The operation is repeated until no more lead coating forms. The object is first washed in water and

⁹ *Electrochem. & Met. Ind.* (1909), 7, 440.

¹⁰ *Journ. Ind. & Eng. Chem.* (1911), 3, 239.

¹¹ *Loc cit.*

then in alcohol, after which it is dried and weighed. Or the lead may be determined by dissolving in nitric acid and titrating with potassium dichromate.

COMMENTS ON THE LEAD ACETATE METHOD

In the original paper it is recommended that a square (5.08 by 5.08 centimeters), which should not vary more than 0.04 centimeter ($\frac{1}{4}$ of an inch) plus or minus, be used for the test. This is too small a piece to give accurate results under ordinary conditions. If two such squares are cut so that on each side of the first there is an error of plus 0.04 centimeter, and on each side of the second an error of minus 0.04 centimeter, the total error will amount to over 6 per cent. It is practically impossible to cut sheeting as accurately as this with ordinary shears, and a great many pieces are tested with errors much greater. Some of the pieces cut by power shears are not sufficiently accurate.¹² Another and more serious reason against the use of such small pieces is that they do not give a fair average of the composition of the material. Any variation in the coating is, of course, multiplied by thirty-six in calculating the results to the basis of 900 square centimeters.

That the variation in coating may be considerable was demonstrated by some tests made in this laboratory. The results are shown in fig. 1. The maximum variation was 2.19 grams per 15-centimeter square, or about 12.3 per cent. This is equivalent to 8.76 grams per 900 square centimeters, or about 0.3 ounce per square foot. It is easy to see that had only the small squares been used a great error would have been possible, leaving out of consideration any inaccuracies in cutting. Nothing smaller than 15-centimeter squares should be used for testing galvanized sheeting, and when convenient 30-centimeter squares are to be recommended. All tests made in this work by the lead acetate methods have been with 15-centimeter squares, so that average results might be obtained. Such a procedure is satisfactory for experimental purposes, but would be too expensive for a laboratory where a great many tests are made.

Theoretically, to remove the zinc from a 15-centimeter square of galvanized iron containing 68.8 grams of zinc per 900 square centimeters, about 100 grams of lead acetate $[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}]$ would be required. In practice, however, it has been found

¹² These considerations are intended to apply to commercial testing only. Of course, for experimental purposes, it is possible to prepare squares having negligible variations in size, but this requires considerable time and is not practicable for routine work.

that considerably more than this amount is necessary, because the solution becomes exhausted long before all the lead has been removed. Three causes for this may be suggested.

1. The concentration of the lead ions is diminishing.
2. The concentration of the zinc ions is increasing.
3. The removal of the alloy layers is much slower than that of the zinc itself. As a result the reaction almost ceases unless there is a large excess of lead acetate present.

In order to determine the effect of each of these factors, the

Rejected portion.				
18.84	18.95	18.17	18.94	20.08
18.19	18.34	—	—	18.85
18.50	—	19.57	18.93	19.79
17.89	18.40	18.20	18.38	19.00

FIG. 1. A galvanized sheet was taken at random. A piece was cut 60 by 75 centimeters, rejecting the portion at the end and sides. This was then cut into squares 15 by 15 centimeters, and each was numbered so that its original position on the sheet might be known. The numbers in the diagram show the weight of coating in grams found on each square. The squares were cut accurately, so that the variation in results is almost entirely due to variation in the coating itself.

following experiments were carried out. One of the 15-centimeter squares was placed in a quantity of lead acetate solution containing the theoretical amount of lead necessary to replace the zinc, and although it was left for a number of hours, with frequent removals for cleaning off the precipitated lead, not all the zinc was removed. The action did not altogether cease, but was so slow that it was worthless. On analysis this nearly exhausted solution was found to contain 57.05 grams lead acetate per liter.

Another portion of lead acetate solution was subjected to immersions of fresh galvanized sheets until no more action could

be noticed on the last one, even after several hours. The essential difference between this and the previous experiment was that in this case the solution was always acting on zinc rather than on any of the zinc-iron alloys. It might be expected that more of the lead could be removed. This was found to be true, for the analysis showed 2.62 grams lead acetate per liter.

A lead acetate solution which contains no zinc ions can be still more dilute and attack a galvanized surface. Some of the original solution was diluted to various concentrations with distilled water, and each was tried with a fresh piece of galvanized iron. A solution containing only 0.5 gram lead acetate per liter showed some action. This may be made clearer by summing up the results.

TABLE I.—Minimum strength of active lead acetate solution under various conditions.

Condition.	Lead acetate per liter. Grams.
Solution containing no zinc ions and acting on outer zinc coating	0.50
Solution containing zinc ions and acting on outer zinc coating	2.62
Solution containing zinc ions and acting on the zinc-iron alloys	57.05

These results indicate that each of the three factors mentioned above has its effect on rendering the acetate solution inactive. It is likely that the relative importance of each varies with the temperature, concentration of the solution, and character of the zinc-iron alloys. However, the net result is that more than the theoretical amount of lead acetate is required, and consequently the cost of each test is increased.

THE HYDROCHLORIC ACID METHOD

Hydrochloric acid¹³ may be used for removing the coating from galvanized iron if the temperature and concentration are kept within certain limits. A solution made from one part

¹³ After the present paper had been completed, I received an abstract of a paper by Aupperle [*Metal Ind.* (1915), 13, 329; *Iron Age* (1915), 96, 132]. Aupperle uses hydrochloric acid having a density of 1.20, containing a small amount of antimonous chloride. The samples are cut 5.72 by 5.72 centimeters (2.25 by 2.25 inches). He objects to the Preece test, because of its unreliability, and to the lead acetate method, because of the long time required.

The results obtained in this laboratory show that if a lower density of acid is used no addition of any salt is necessary. The disadvantages of such small pieces have already been discussed.

(by volume) of chemically pure hydrochloric acid to one part of distilled water should be employed. Such a solution has a density of approximately 1.098 at 15.5°C. and contains 19.53 per cent acid. The temperature of the acid should never be higher than 45°C. A 15-centimeter square (or larger piece) of galvanized sheet is weighed, placed in the acid, and allowed to remain until perceptible effervescence ceases, which should require only two or three minutes. It is then removed and washed. If any zinc still remains, the sheet is again placed in the acid until this is dissolved, which usually requires only a minute or two. It is removed, washed in water, then in alcohol, placed in a drying oven for a few minutes, cooled in a desiccator, and weighed.

Preliminary tests convinced me several years ago that this is a very satisfactory method, but at that time no detailed investigation was undertaken. The fact that iron dissolves so readily in hydrochloric acid under some conditions would lead one to think that the acid was not suitable for this purpose. However, the present work shows that no iron (except, perhaps, a trace) other than that alloyed with the zinc goes into solution, provided the temperature and density of the acid are properly controlled.

COMPARISON OF THE LEAD ACETATE AND HYDROCHLORIC ACID METHODS

Preliminary experiments showed that in both methods some iron was removed from the sample. In the lead acetate method this iron comes entirely from the zinc-iron alloys, because the basic lead acetate solution does not attack the iron base. A number of tests were run to determine if the same thing was true with the hydrochloric acid. Variations had been noticed in results obtained by both methods, and it was desired to determine whether these were due to errors in the methods or to lack of uniformity in the coating itself. Consequently, in every case after the coating had been removed, the solution and all wash waters used in the operation were placed in a flask, made up to volume, and the iron and zinc were determined in an aliquot portion.

This operation was found to be much simpler in the hydrochloric acid than in the lead acetate solution. In the latter case the first analyses were made by simply pipetting off the solution from the metallic lead. This gave results which were incorrect. Approximately 50 per cent of the zinc had been absorbed by the metallic lead. It was found necessary first to

decant the solution from the lead and then to heat the latter with sulphuric acid until it was completely disintegrated. After cooling, the mixture was added to the solution which precipitated all the lead as sulphate. The new mixture was then cooled, transferred to a 2-liter flask, and made up to volume. The lead sulphate settled completely, and portions of the clear solution were withdrawn and analyzed. The iron was precipitated with ammonia and determined gravimetrically. The zinc was determined by titration with potassium ferrocyanide.

In the hydrochloric acid solution it was only necessary to oxidize the iron with nitric acid, add some ammonium chloride, and then precipitate with ammonia.

Tables II and III show the results obtained by the two methods.

TABLE II.—By hydrochloric acid method.*

No.	Initial temperature.	Final temperature.	Total loss in weight.	By analysis.			Calculated to ounces per square foot.			
				Zinc (a).	Iron (b).	$\frac{b}{a+b}$	Zinc by analysis.	Iron by analysis.	Total Zn+Fe by analysis.	Total loss in acid.
	°C.	°C.	Grams.	Grams.	Grams.	Per cent.				
1	31	45	17.6155	16.9289	0.7583	4.29	2.45	0.11	2.56	2.56
2	30	45	18.3519	17.5152	0.7757	4.26	2.55	0.11	2.66	2.67
3	30	45	19.4566	18.6183	0.7828	4.00	2.71	0.11	2.82	2.83
4	30	43	17.6164	16.9879	0.7583	4.29	2.46	0.11	2.57	2.56
5	30	44	17.7744	17.1068	0.7271	4.08	2.49	0.11	2.62	2.59

* The hydrochloric acid solution contained 19.58 per cent HCl (density, 1.098). A separate portion (400 cubic centimeters) was used for each sample. All samples were 15 by 15 centimeters and were cut from the same sheet, washed in benzol, dried, and weighed.

Column four shows the loss of weight suffered by each sample in the hydrochloric acid. These values multiplied by four give grams per 900 square centimeters. The acid solution was analyzed for iron and zinc. These results are shown in columns five and six. The last two columns show the very close agreement between the total zinc and iron determined by analysis and the total loss in acid.

TABLE III.—By lead acetate method.*

No.	Temperature.	Total loss in weight.	By analysis.			Calculated to ounces per square foot.			
			Zinc (a).	Iron (b).	$\frac{b}{a+b}$	Zinc by analysis.	Iron by analysis.	Total Fe+Zn by analysis.	Total loss in lead acetate.
	°C.	Grams.	Grams.	Grams.	Per cent.				
1	30	17.3354	16.9007	0.5698	3.26	2.46	0.08	2.54	2.52
2	30	17.8257	17.3119	0.7217	4.00	2.52	0.10	2.62	2.59
3	30	18.4110	17.8625	0.6105	3.30	2.60	0.09	2.69	2.68

* Fifteen-centimeter squares cut from the same sheet as those used in the hydrochloric acid method were placed in 500 cubic centimeter portions of lead acetate solution. No appreciable rise in temperature took place.

It is evident that the results obtained by use of hydrochloric acid are accurate. The amount of iron dissolved, in terms of ounces per square foot, is a constant to two decimal places. Analytical results check those obtained by the acid method, and the amount of iron dissolved varies but slightly from that in the lead acetate. That slightly less iron is removed by the lead acetate may be explained by the fact that the acetate does not dissolve all of the zinc-iron alloys. This may also explain why the results of the iron determinations in the acetate solution are not so uniform as those in the acid solution. A square of galvanized iron which had been stripped in lead acetate was washed and then placed in hydrochloric acid for some minutes. On analysis it was found that both iron and zinc had been dissolved from the plate. However, it may be said that while the presence of the zinc is of experimental interest it was not present in sufficient amount seriously to affect the results.

EFFECTS OF CONCENTRATION AND OF TEMPERATURE

In using hydrochloric acid for removing zinc from galvanized iron, some attention must be paid to the concentration and temperature. Also it is obvious that an iron sheet should not be left in the acid longer than is necessary to remove the last of the zinc. These factors may be easily controlled, and the allowable range is so large that the test is perhaps the simplest of any yet published.

In deciding what strength of acid to employ in the work, the most important point is to have an acid that will remove all the zinc and as little iron as possible. Two other factors to be considered are the speed with which the acid dissolves the zinc and the rise in temperature caused by the reaction. Table IV shows the results obtained by using three different concentrations.

TABLE IV.—*Effect of acid concentration.**

No.	Dilution of acid.	Density of acid.	Per cent HCl.	Volume of acid.	Initial temperature.	Final temperature.	Character of reaction.	Total loss (a).		Iron dissolved (b).		b/a.	Zinc dissolved.
								Per 900 square centimeters.	Per sq. foot.	Per 900 square centimeters.	Per sq. foot.		
				c.c.	°C.	°C.		Gms.	Ozs.	Gms.	Ozs.	P.ct.	
1	conc.	1.190	37.58	400	30.0	50.0	Violent...	73.3449	2.67	4.1205	0.15	5.62	All.
2	1-1..	1.098	19.55	400	30.0	41.5	Medium..	73.3449	2.67	3.0217	0.11	4.12	Do.
3	1-3..	1.052	10.55	400	33.5	40.0	Slow.....	71.1473	2.59	3.0217	0.11	4.25	Do.

* Each sheet was 15 by 15 centimeters.

The choice of the most satisfactory concentration is easily made. The action of the concentrated acid is too violent and results in dissolving some iron from the base. For that reason it may be eliminated. The other two concentrations are equally adapted to the work in that they both remove all the zinc with the minimum amount of iron. Since the 1.098 density acid acts more rapidly than the other and apparently has no disadvantage, it is considered the best. It is possible that an acid might be found some place between densities 1.098 and 1.190 which would act more rapidly without dissolving any more iron, but the former seems to answer every requirement. It is also possible that with some grades of galvanized iron it might be better to use a slightly weaker acid.

Having determined the best concentration of acid, it was next necessary to investigate the influence of temperature on the solution velocity of the iron base. Previous experiments had shown that if a 15-centimeter square of sheeting were left in the acid at room temperature for many minutes the loss in weight was negligible. This work was extended to include temperatures between 30° and 100°C. Each piece was left in the acid (at a given temperature) for twenty minutes, removed, washed in water and then in alcohol, and finally dried and weighed. The test was purposely made very severe to guard against any possible errors. Removal of zinc from a sheet does not require as much as ten minutes. No attempt was made to keep the temperatures exact by a thermostat, because such refinements are unnecessary in the actual tests. Fifteen-centimeter squares were used. The following results were obtained.

TABLE V.—*Effect of temperature on solution velocity of iron base.*

Strength of acid.	Temperature.	Loss in weight.	Loss.	Calculated to ounces per square foot.
Density.	°C.	Grams.	Per cent.	
1.098	30	0.0339	0.03	0.006
1.098	45	0.0494	0.05	0.007
1.098	60	0.0921	0.09	0.013
1.098	80	1.3256	1.26	0.193
1.098	100	6.1648	5.93	0.897

The temperature of the acid may run up to 60° without causing any appreciable error, but since there is no reason for

such a high temperature, it is recommended that the solution be kept at 45° or below.¹⁴

CRITICISM OF AN ANALYTICAL METHOD SOMETIMES USED

Some chemists use an analytical method for determining the zinc, which is as follows:

A 30-centimeter square of the original material is weighed, and the weight is recorded. A few small pieces are then cut and weighed on an analytical balance, and the percentage of zinc is determined by analysis. The weight of the large square in grams is then multiplied by this factor to give grams of zinc in that area. Such a procedure is, of course, erroneous. The present work has shown that the galvanizing on one sheet 60 by 75 centimeters may vary as much as 8.76 grams per 900 square centimeters (fig. 1).

A SIMPLE AND RAPID METHOD FOR DETERMINING IRON

Any solution which will remove all the zinc from a piece of galvanized iron will also remove the iron in the zinc-iron alloy. If the zinc is then calculated from the loss in weight, there will be an error due to the iron that has been dissolved. This error is comparatively so small that it is usually disregarded. However, it is sometimes desired to correct it, and this may be accurately done by precipitating the iron with ammonia and weighing as the oxide.

The iron may be determined approximately by a much simpler procedure. The results are not so accurate, but are sufficiently so for most purposes. While the coating is being dissolved by the acid, the iron in solution is being reduced by the nascent hydrogen, and the rise in temperature aids the reaction. The tray in which the test is made should be nearly covered, with only a small outlet for the evolved gases. The minimum volume of acid should be used—about 350 cubic centimeters. As soon

¹⁴ In practice it is not necessary to use a separate portion of hydrochloric acid for each sample. In using any method for the first time, or in testing a brand of galvanized iron with which he is unfamiliar, it is well for a chemist to determine the alloyed iron and the loss in weight of the stripped sheet in the testing solution. For routine tests the hydrochloric acid is placed in a jar or crock which is large enough to accommodate one or more pieces of the galvanized iron (without touching each other). This same acid may be used for a number of samples until the action becomes too slow on account of the low concentration of hydrogen ions. The only necessary precaution is to observe the temperature from time to time and not allow it to exceed 45°C.

as the coating has entirely disappeared, the sheet is removed and rinsed, allowing the water to run into the tray. The contents of the tray are then rapidly transferred to a large beaker, containing from 400 to 500 cubic centimeters of recently boiled water and about 100 cubic centimeters of titrating solution.¹⁵ The iron is then titrated with fifth normal permanganate (using a 100 cubic centimeter burette). The error in such a determination is probably due to the fact that a portion of the iron is oxidized by contact with the air before the titration is made and that the comparatively high concentration of hydrochloric acid present interferes to some extent with the end point. This determination requires less than five minutes, while the gravimetric method requires from one to two hours.

VARIOUS BRANDS TESTED

All results given above were obtained by tests on samples cut from the same large sheet of galvanized iron. This was done so that the samples might be as nearly uniform as possible and thus afford a sound basis of comparison. It was realized, however, that the method would be worthless unless it would give equally satisfactory results with products of various mills. Accordingly the test has been applied to five different brands of galvanized sheeting. Four of them were made in the United States and one in England. Two squares were cut from each sheet, properly cleaned and weighed, and the total loss in hydrochloric acid was determined. In each case, after the square was removed, the acid and washing were placed in a liter flask, made up to the volume and were analyzed for iron by the gravimetric method. The stripped squares were then placed in hydrochloric acid and allowed to remain for twenty minutes. They were removed, washed, dried, and reweighed.

It is evident that the iron dissolved from the base itself is negligible. This is true in all the results given in this paper as well as in a number of other brands which have been tested from time to time. The alloyed iron is nearly always less than the minimum variation of the coating between samples of the same sheet and can usually be neglected. It seems peculiar that the total alloyed iron per square foot for all the brands tested should be so uniform, when there is such a wide variation in total coating.

¹⁵ See Olsen, J. C., *Quantitative Chemical Analysis*. D. Van Nostrand Co., New York (1908), 319.

TABLE VI.—Tests on various brands of galvanized iron by the hydrochloric acid method.*

Brand No.	Total loss in weight. (a)	Iron dissolved with zinc. (b)	b/a.	Iron dissolved from stripped sheet.	Total loss per square foot.	Iron in coating per square foot.	Iron dissolved from stripped sheet per square foot. ^c	Initial temperature.	Final temperature.
	Grams.	Grams.	Per cent.	Grams.	Ounces.	Ounces.	Ounces.	°C.	°C.
1 b	18.179	0.7826	4.29	0.035	2.56	0.11	0.005	31	45
	18.939	0.8036	4.26	0.034	2.67	0.11	0.005	30	45
2	17.790	0.8050	4.53	0.035	2.51	0.11	0.005	29	40
	18.880	0.8638	4.57	0.020	2.66	0.12	0.003	29	40
3	20.571	0.6210	3.02	0.043	2.90	0.09	0.006	29	40
	17.680	0.4724	2.67	0.030	2.49	0.07	0.004	29	42
4	11.259	0.5012	4.54	0.036	1.58	0.07	0.005	29	38
	13.170	0.5670	4.30	0.030	1.86	0.08	0.004	29	40
5	18.026	0.6608	3.63	0.059	2.54	0.09	0.008	30	41
	20.356	0.7350	3.61	0.089	2.87	0.10	0.013	30	43

* Density of the acid, 1.093.

b Brand used in all previous tests.

c At end of twenty minutes. The stripped sheets were placed in acid of the same density, at 35°. In this case the action was so slight that there was no appreciable rise in temperature. Each sample was 15.25 by 15.25 centimeters.

A study of Table VI reveals the following:

BETWEEN TWO SAMPLES OF THE SAME BRAND.

	Grams per 900 square centimeters.	Ounces per square foot.	Brand No.
Minimum difference in coating.....	2.9397	0.11	1
Maximum difference in alloyed iron.....	0.5944	0.02	3
Maximum difference in iron dissolved from stripped sheet*.....	0.1418	0.005	5

BETWEEN TWO SAMPLES OF DIFFERENT BRANDS.

	Grams per 900 square centimeters.	Ounce per square foot.	Brand No.
Maximum difference in coating.....	37.2480	1.32	3, 4
Maximum difference in alloyed iron.....	1.5256	0.05	2, 3
Maximum difference in iron dissolved from stripped sheet.....	0.2835	0.01	2, 5

* In all brands tested, except No. 5, this difference is negligible when temperature, concentration of acid, and time are uniform.

THE REACTION BETWEEN HYDROCHLORIC ACID AND GALVANIZED IRON

These measurements were made with the object of obtaining a clearer idea of just what happens when a galvanized sheet

is subjected to the hydrochloric acid test. It is evident that the removal of the zinc is more uniform than with either copper sulphate or lead acetate solutions, because there is no metallic deposit to interfere.

As long as only the outer layer of nearly pure zinc is exposed to the action of the acid, the rate of solution should remain almost constant.¹⁸ The surface exposed remains about uniform, and since the acid is present in considerable excess, the change in concentration is not great. The results show that this is true.

Manipulation.—A sheet of galvanized iron 7.6 by 30.6 centimeters was bent into the form of a cylinder and placed in a large beaker. The edges were suitably protected. The apparatus was fitted with a stirrer, and 1 liter of hydrochloric acid (density, 1.052) was rapidly poured in. At intervals of one minute 25 cubic centimeters of the acid were removed for analysis. Effervescence had apparently ceased by the end of the sixth minute, but the reaction was allowed to run ten minutes. After ten minutes the iron was removed and found by analysis to be free from coating.

Table VII shows the results. The iron was determined gravimetrically, and the zinc was titrated with potassium ferrocyanide. The results were calculated to total weight of iron and zinc dissolved in terms of ounces per square foot.

¹⁸ In a heterogeneous system, such as hydrochloric acid and zinc, the velocity of the reaction may be expressed by the equation $dx/dt = kO(a-x)$. Here O represents the area of the exposed surface

a , the original concentration of the acid

x , the decrease in concentration of the acid caused by x equivalents of metal going into solution in the time t . [See Nernst, W., *Theoretical Chemistry*. Macmillan & Co., London (1911), 584.]

In the present work a large excess of acid was used, so that the concentration remained practically constant. It can be assumed that the total surface remains constant. Therefore, theoretically the right member of the equation becomes a constant, or $dx/dt = K$. This condition cannot be realized exactly, however, because of other factors which affect the velocity. In the first place no attempt was made to keep the temperature of the acid constant. In actual practice there is a rise in temperature, and it was desired to keep conditions as nearly similar as possible. Each zinc-iron alloy has its velocity constant and each has its velocity equation, $dx/dt = kO(a-x)$. Therefore, as the reaction proceeds and various alloys are exposed, it becomes more and more complex. The surface, O , for some of the alloys is not a constant because usually the entire surface is not exposed at the same time. While the outer coating of zinc is being dissolved, the reaction comes nearest to the theoretical.

TABLE VII.—Zinc and iron dissolved from a sheet of galvanized iron, minute by minute.

[Initial temperature, 30.5° C.; final temperature, 37.5° C.; volume of acid, 1,000 cubic centimeters; concentration of acid, 10.55 per cent HCl.]

Time.	Total zinc.	Total iron.	Zinc per square foot.	Iron per square foot.	$\frac{\text{Fe}}{\text{Zn} + \text{Fe}}$
Min.	Grams.	Grams.	Ounces.	Ounces.	Per cent.
1	4.3280	0.0280	0.6102	0.0039	0.64
2	12.0812	0.0924	1.7034	0.0130	0.76
3	15.4214	0.1760	2.1744	0.0251	1.51
4	16.6165	0.5224	2.3429	0.0737	3.05
5	16.8109	0.5728	2.3703	0.0808	3.30
6	16.8109	0.6586	2.3703	0.0929	3.77
7	16.8245	0.6967	2.3723	0.0982	3.98
8	16.8278	0.7313	2.3727	0.1031	4.16
9	16.8502	0.7358	2.3769	0.1037	4.18
10	16.8998	0.7358	2.3828	0.1037	4.18

These values were used in plotting the solution velocities of the zinc and the iron against the time (fig. 2).

Discussion of results.—The iron in a hot-galvanized sheet is present as follows:

1. The spelter itself before being placed in the bath contains traces of iron.

2. The spelter is gradually contaminated with iron from the walls of the bath and from iron sheets or other articles that are passed into it.

3. Alloys are formed on the immersed sheet by the action of the molten zinc.

4. The base is, of course, nearly all iron.

The various steps in the action of hydrochloric acid on a galvanized plate may be clearly seen from the results. The acid at first comes into contact with the zinc, which contains only the iron present in the spelter when the sheet was placed in the galvanizing bath. The reaction is very rapid, and during the first three minutes 91.25 per cent of the total zinc present passes into solution. During the same period only 24.20 per cent of the total alloyed iron dissolves. During the next three minutes 8.22 per cent more of the zinc and 65.38 per cent more of the iron dissolve. The remainder of the time the reaction is very slow, only 0.53 per cent of zinc and 10.42 per cent of the iron being dissolved. The great variation of the percentage of iron in the total metal dissolved is given in the last column of the table. Still greater variation is observed if the percentages

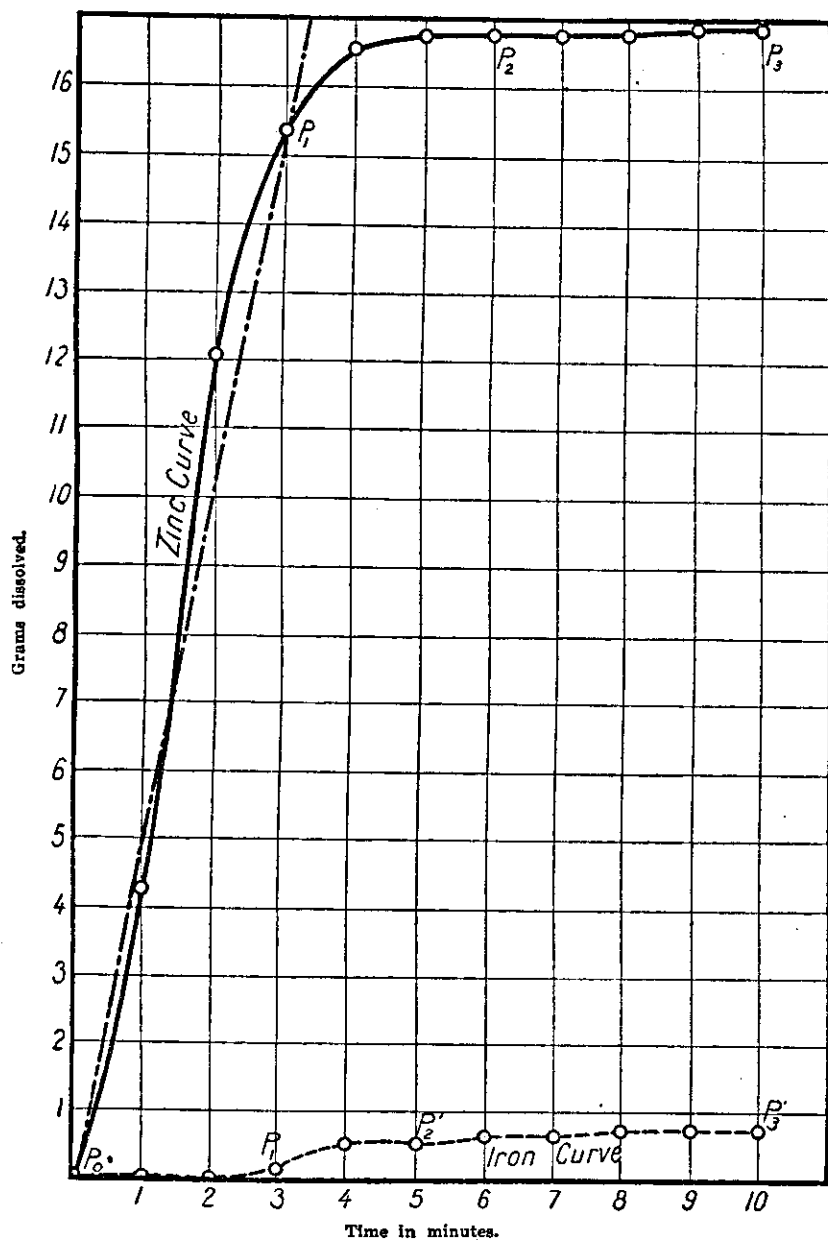


FIG. 2. Solution velocity of galvanized iron in hydrochloric acid.

are calculated separately for different minutes. For instance, during the first minute the iron is only 0.64 per cent of the total metal dissolved. During the fifth it is 20.29 per cent; in the seventh, 84.86 per cent; in the eighth, 91.32 per cent. This work seems to indicate that, in addition to alloys like FeZn_8 and FeZn_{11} , there may be a series high in iron and low in zinc, such as Fe_7Zn and Fe_{11}Zn .

On the zinc curve, from P_0 to P_1 , the acid is dissolving the outer coating of almost pure zinc and the curve is nearly a straight line. From P_1 to P_2 the velocity falls off rapidly because the zinc coat has almost disappeared and the alloys are exposed. On the iron curve the maximum rise is between P'_1 and P'_2 , or after the zinc is almost completely dissolved.

As has been stated, the iron dissolved during the first few minutes is due to the iron contamination of the molten zinc before the sheet is placed in the bath. It is true also that during that time the acid may have gone entirely through the outer layer of zinc at some point and started acting on one of the zinc-iron alloys. Therefore, if we know the amount of iron dissolved during the first stage of the reaction, or up to the point of the break in the zinc curve, P_1 , we have a hint as to the value of the sheet to withstand corrosion. A high iron content would show that the iron contamination of the spelter is considerable, or that the zinc coating is thin in spots. Either condition would indicate that the sheet is of inferior quality. It is obvious that the outer zinc coating should be as uniform as possible, and that the purer it is, the better. On the other hand, a very small amount of iron removed during the first stage of the reaction would assure both the purity and the uniformity of the outer coating. I propose to investigate this question further and to attempt to determine the maximum percentage of iron that is allowable in a good quality of galvanized sheet under these conditions. Such a test would be simple to carry out, but important.

CONCLUSIONS

1. A hydrochloric acid solution gives satisfactory results for determining the amount of the coating on galvanized iron. Directions for its use are given. These include the concentration of the acid, the temperature, and the size of the test piece.
2. The accuracy and reliability of the test have been proved in a number of ways. It requires little labor and is rapid and inexpensive.
3. A convenient method is given for correcting for the alloyed

iron dissolved by the acid in case such correction is deemed necessary.

4. Measurements of the solution velocity of galvanized iron in hydrochloric acid have been made. The results indicate that the system of zinc-iron alloys is very complex. From the solution-velocity time curves, an approximate idea of the uniformity and purity of the zinc coating may be obtained.

5. In investigating the value of various methods for testing galvanized iron, it is necessary to know (a) how much iron is dissolved from the base and (b) whether or not any zinc in the form of zinc-iron alloys remains undissolved. Without these data it is impossible to get the proper basis of comparison.

ILLUSTRATIONS

TEXT FIGURES

- FIG. 1. Diagram, showing method of sampling a sheet of galvanized iron.
2. Chart, showing the solution velocity of galvanized iron in hydrochloric acid.

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COMMENTS ON THE ANALYSIS OF BABBITT METAL¹

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The analysis of Babbitt metal has always offered considerable difficulty to chemists, particularly those who are engaged in commercial testing. Although many excellent papers have been published on the subject, most of the methods given are either too long and involved for commercial purposes, or else they are not sufficiently accurate and reliable in the hands of the average analyst. There has been a wonderful advance in electrolytic analysis, and many of the methods now being published are along these lines. While this system is very close to the ideal with the right equipment, there are many laboratories doing general chemical work where the expense of installing suitable electrical equipment is hardly justified.

There is scarcely any other material which has so large a range of composition as Babbitt metal. The lead or the tin content may vary from 0 to 90 per cent, and there is often a great variation in the other elements present. Some of the varieties have special names, but as a rule the average consumer calls almost any white metal used for antifriction purposes a babbitt. Besides the metals actually called for in the formula, there are invariably impurities present which in some cases are in sufficiently large amounts to cause trouble in the analysis. Persons submitting such samples seldom seem to realize that while some samples are simple others are exceedingly difficult and cannot be completed without a great deal of labor if results are to be dependable.

An object of this paper is to point out that there is no general method that may be equally well applied to all samples. Many methods are published which show accurate results with one class of babbitts, but fail with others. Until a good general method is devised, the chemist must keep well in mind the limits of whatever method he may favor and be constantly on the alert to modify it to suit the circumstances, or to substitute a different one if necessary.

The present work has been done with babbitts having the

¹ Received for publication September 9, 1915.

following composition: Lead, 85 to 90 per cent; antimony, 10 to 15 per cent; tin, 0 to 5 per cent; copper, 0 to 1 per cent. The methods of analysis which I have found most satisfactory and which are intended to apply to this class of alloys in particular are as follows:

ANTIMONY

The method of Walker and Whitman² for antimony, which is a modification of Low's³ method, has been closely followed except for the changes which are noted. The method as given by them⁴ is as follows:

To 1 gram alloy in a 450 cc. Erlenmeyer flask, add 10-15 cc. strong sulphuric acid, and heat on hot plate until alloy is thoroughly decomposed. This is generally accomplished in about 30 minutes from the time fumes of SO₂ begin to be given off. Cool, add 200 cc. water and 20 cc. strong hydrochloric acid, boil to make sure that all SO₂ is driven off, cool and titrate rapidly with potassium permanganate which has been standardized against metallic antimony. The true endpoint is when a pink color shows after agitating the liquid, though this pink will very soon disappear.

In carrying out this method, difficulty is often experienced in obtaining a sharp end point, and some chemists have never used it to any extent on that account. However, a sharp end point can be obtained if the method is modified as follows: Use a 300 cubic centimeter Jena-glass Erlenmeyer flask for digestion and dilute to about 150 to 175 cubic centimeters. If after boiling the volume has decreased materially, add sufficient water to replace that which has been evaporated. Cool the solution thus obtained to about 5 or 10°C., and titrate as rapidly as possible, until the end point is nearly reached, then add two or three drops at a time, shaking the flask thoroughly. When a pink color flashes over the entire solution, the end point is reached. These precautions are necessary because the pink color at the end point is not permanent, as in the case of iron titrations, and unless the solution is kept cold and the permanganate added in some definite way for every determination, one is very likely to obtain erroneous results.

The permanganate solution should be standardized frequently. During the titration, if the hydrochloric acid solution is not sufficiently dilute, sometimes the odor of chlorine will be noticed,

² *Journ Ind. & Eng. Chem.* (1909), 1, 520.

³ *Journ. Am. Chem. Soc.* (1907), 29, 66.

⁴ *Loc. cit.*

and the solution will become slightly yellowish. In this case it is best to throw out the determination and start a new one, using slightly less hydrochloric acid, because, under such conditions, the true end point cannot be obtained.

TIN

Walker and Whitman's method for tin has been closely followed, but slight modifications have been found helpful. Their method is as follows:

Treat from 0.2–1 gram of alloy (do not use an amount of alloy containing more than 0.2 gram tin) in a 450 cc. Erlenmeyer flask with 10–15 cc. strong sulphuric acid, heat on the hot plate until the alloy is thoroughly decomposed, cool, add 200 cc. water, 30 cc. strong hydrochloric acid, and about 1 gram of steel turnings, heat and when reduction appears complete, but before the last particles of steel have dissolved, place a two-hole rubber stopper in the neck of the Erlenmeyer flask—one hole of the stopper should carry a tube reaching below the surface of the liquid, the other hole should carry the short arm of a bent tube, the long arm of which reaches nearly to the bottom of a 100 cc. Erlenmeyer flask containing a solution of sodium bicarbonate. This small Erlenmeyer is held on the bent tube by a cork which has a notch cut in it to act as a vent. Through the tube reaching below the surface of the liquid in the large Erlenmeyer pass a current of carbon dioxide, heat to boiling until all steel is dissolved, continue passing CO_2 and cool as quickly as possible; loosen stopper but let current of CO_2 continue, add cautiously some starch solution and titrate with $N/10$ iodine. It is necessary to absolutely exclude air and to standardize the iodine solution with pure tin. Results are accurate.

I find this method very satisfactory up to the point where the solution is boiled with 1 gram of steel turnings.

Walker and Whitman recommend the use of steel turnings for the reduction of tin, but give no details concerning the kind of steel or the size of the drillings which are best suited to the work. This is likely to give one the impression that any steel drillings which may be around the laboratory may be used. This is not true if it is desired to obtain the most rapid and most accurate results. Some steels are more suitable than others. For instance, a steel high in phosphorus is to be avoided. In general, a mild, open-hearth steel is best suited to the work. In order to complete the reduction in a comparatively short time, the steel drillings should be small and uniform in size. By using uniform drillings, the time of reduction is known within a very few minutes, and the work can be planned and carried out accordingly. The steel which I have found to give the most satisfactory results contained about 0.12 per cent carbon. The drillings were placed on a 40-mesh sieve, and only the portion passing the sieve was preserved for use.

The fine particles passing an 80-mesh sieve were rejected. A considerable quantity of these drillings was prepared and after thorough mixing was preserved for use in babbitt analyses. The uniformity of the drillings, both in size and composition, was a very helpful factor.

The troublesome part of this method for tin is in making the titration. The antimony compounds present have been reduced to metallic antimony, which is present as a black, flocculent precipitate. This is most troublesome with a sample which is high in antimony and low in tin, in which event it is usually necessary to allow the precipitate to settle after each addition of iodine before the presence of the blue color of the end point can be distinctly seen. Another disadvantage is that the precipitate is likely to conceal small pieces of undissolved steel, which would, of course, cause high results.

To avoid this remove the antimony by filtering the boiling-hot solution through a coarse filter paper and wash several times with hot water. If the solution is not filtered while very hot, lead chloride will crystallize out and interfere with the operation. Receive the filtrate in a 300 cubic centimeter Erlenmeyer flask, add 0.5 gram of steel drillings, and proceed with the method in the regular way. Cool the flask by placing it in a beaker of cold water, being careful to have a vigorous stream of carbon dioxide passing in order to compensate for the vacuum caused by the condensation of the steam in the flask. If a few flakes of antimony appear during the second reduction, they may be disregarded, since by removing the bulk of the antimony the object has been attained.

LEAD

Considerable difficulty was encountered in finding a method for the determination of lead which was accurate and at the same time sufficiently rapid for routine babbitt analysis. Most of the methods which I have tried from time to time failed in one of these two respects. A modification of the method used by Alexander^{*} in the analysis of lead ores has given very satisfactory results. The following solutions are needed:

Ammonium molybdate, 4.25 grams per liter.

Acid ammonium acetate:

Ammonia, 400 cc.

Water, 450 cc.

Concentrated acetic acid, 400 cc.

Tannic acid; one part of solid to 300 parts of hot water.*

* This solution should be made fresh whenever used.

^{*} *Eng. & Min. Journ.* (1893), 55, 293.

Chemically pure metallic lead or lead sulphate should be used for standardizing the ammonium molybdate solution. Weigh the lead with the sample and carry through in parallel. Place 1 gram of the alloy in a 250 cubic centimeter beaker and add 30 cubic centimeters of 1.20 specific gravity nitric acid. After the acid has boiled down to about 10 or 15 cubic centimeters, dilute with 30 to 40 cubic centimeters of water and boil the mixture for ten minutes. After allowing the precipitate to settle, decant the liquid through a filter paper to which has been added a little paper pulp and wash the filter two or three times with 1 per cent hot nitric acid. Treat the precipitate which remains in the beaker a second time with acid and water and filter as before.* After transferring the precipitate to the filter, wash it eight or ten times with dilute nitric acid, taking care to keep the volume of the filtrate and washings down to about 150 to 200 cubic centimeters. Evaporate very carefully to 20 or 30 cubic centimeters and cool. Add excess sulphuric acid and heat the mixture until the water has been expelled and white fumes appear. Dilute with 50 cubic centimeters of water and allow the lead sulphate precipitate to settle. Filter out the precipitate and wash thoroughly with very dilute sulphuric acid. Place the filter paper containing the precipitate in the original beaker and dissolve in 75 cubic centimeters of hot ammonium acetate solution and an equal volume of hot water. When the solution is complete, titrate with ammonium molybdate solution, using tannic acid as an outside indicator. It is very important that the lead solution should be almost boiling at the beginning of the titration to insure complete precipitation of the lead; otherwise it is easy to get a false end point and report wrong results. The standard is titrated in exactly the same way, and a blank is run on the ammonium acetate solution. To determine the value of the ammonium molybdate solution in terms of lead, the weight of the lead in grams, in the standard, is divided by the number of cubic centimeters of ammonium acetate solution used in the titration of the standard, minus the blank titration. This method seems long, but not much time

*This second treatment with dilute nitric acid is very important and should never be omitted. Experiments have shown that after only one treatment with acid, considerable lead nitrate remains with the precipitate and cannot be completely washed out with dilute nitric acid.

It is also important not to evaporate the solution almost to dryness (as is done in the case of determining tin as stannic oxide), for not all of the lead will remain in solution. In case traces of antimony and tin go into solution, they do not interfere with the titration.

is required for the actual operations. I have never had much success in determining lead as chloride according to Walker and Whitman's method, or in determining it directly as sulphate as suggested by Demorest.⁷

COPPER

In many babbitts the copper content is less than 0.5 per cent. In this case a colorimetric method has been found to be sufficiently accurate. It is best to use as a standard a babbitt of known copper content. Weigh equal portions of the standard and sample and dissolve in a small quantity of nitric acid of 1.20 specific gravity. After diluting with about 10 cubic centimeters of water, neutralize with ammonia and add about 5 cubic centimeters in excess. After cooling, dilute the solutions to definite volume, 25 or 50 cubic centimeters, and filter into color carbon tubes having large diameters. By diluting as in the method of reading color carbons, the percentage of copper may be estimated. If a precipitate forms on diluting a solution of the sample or standard, it should be filtered out, using a dry filter, before making a final reading. If the copper exceeds 0.5 per cent, it may be determined by some modification of the cyanide method or the iodide method of Low.⁸ The former is more satisfactory if the percentage of copper is low, while the latter is better for a higher percentage.

IRON AND ZINC

Iron is present in practically all babbitts, although usually the percentage is less than 0.1. To determine the iron, the filtrate from the lead sulphate may be utilized. Dilute this filtrate to about 300 cubic centimeters, heat to boiling, and saturate with hydrogen sulphide. If any precipitate is formed, filter and wash with hot hydrogen sulphide water. Partly evaporate the filtrate to expel the gas and boil with the addition of a few drops of nitric acid. Precipitate the iron by neutralizing with ammonia and determine as ferric oxide.

As a rule zinc is present in only small amounts—usually less than 0.1 per cent. It may be determined in the filtrate from the iron.

PREPARATION OF A STANDARD BABBITT METAL

The standardization of the various volumetric solutions mentioned above may be advantageously effected by the use of stand-

⁷ *Journ. Ind. & Eng. Chem.* (1913), 5, 842.

⁸ *Journ. Am. Chem. Soc.* (1896), 18, 458.

ard babbitts. A set of several such standards corresponding in general composition to the samples usually submitted for analysis should be on hand and that one selected which closely corresponds to the composition of the sample. As is well known, it is difficult to prepare a babbitt which is sufficiently homogeneous to serve as a standard. As a rule there is considerable segregation of the materials present, but a standard was made for use in connection with this work which was satisfactorily uniform. Pure lead, antimony, tin, and copper were obtained and turned over to an expert in making alloys. The metals were mixed in the following proportions: Lead, 85 per cent; antimony, 12 per cent; tin, 2 per cent; copper, 1 per cent. The alloy was cast in the form of a small cylinder about 3.5 centimeters in diameter by 10 centimeters long. The samples were taken with a hack saw at various points in the cylinder and analyzed separately, in duplicate. The results showed the metal to be uniform. After preparing a quantity of the standard, uniform in fineness and composition, portions may be weighed with the samples and carried through the various operations. Especially in the tin and colorimetric copper determinations it is well to have both standard and sample as nearly as possible of the same composition.

GALVANIZED-IRON ROOFING IN THE PHILIPPINES ¹

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INTRODUCTION

The great loss from fires in the Philippines due to the general use of readily combustible building materials has demonstrated the necessity of substituting noncombustible roofing for the ordinary nipa ² thatch. Tile, slate, and asphalt are so utilized to a limited extent, but galvanized iron is by far the most widely used fire-proof roofing material. In towns of any importance practically all large buildings have galvanized iron roofs. The entire demand for this material is met by import, the following data showing the amount and value of galvanized iron annually brought into the Islands:

TABLE I.—Quantity and value of Philippine importations of galvanized iron.*

Year.	Quantity.	Value.
	<i>Kilograms.</i>	<i>Pesos. ^b</i>
1911.....	8, 179, 955	1, 120, 660
1912.....	10, 095, 640	1, 344, 024
1913.....	10, 075, 956	1, 480, 580
1914.....	10, 520, 233	1, 540, 622
1915.....	5, 698, 927	879, 207
Total.....	44, 570, 711	6, 365, 293

* Data for this table were secured from the *Annual Rep. Bur. Customs for the year ended December 31, 1912* (1913), 117; *ibid.* for 1915 (1916), 97. These figures cover only corrugated sheets. In view of the fact that plain galvanized sheets are included under "all other sheets and plates" in the report, it is not possible to give exact figures for them. Import values for "all other sheets and plates" amounted to ₱520,722 for 1914, of which probably 80 per cent are plain galvanized sheets.

^b One peso Philippine currency equals 50 cents United States currency.

The value of this import gradually increased until it reached 1,540,622 pesos for 1914, but dropped to 879,207 pesos in 1915, a decrease largely due to the advance in price caused by the European war. In view of the material improvements going on in all sections of the Islands, an even greater demand for this roofing material may be expected in the future.

As a result of the great demand for corrugated galvanized sheets various brands of this material have been imported.

¹ Received for publication July, 1916.

² The leaves of the nipa palm, *Nipa fruticans* Wurmb.

These have shown great variations in quality. There have been instances in which new sheets showed marked corrosion when brought from storage. Some brands failed completely after from two to five years of service, while some sheets put in place thirty years ago are in good condition and are still rendering satisfactory service. This striking difference in the behavior of old and certain modern corrugated galvanized sheets under actual conditions of weather exposure, together with the fact that the yearly import of this material represents a considerable financial outlay, led the Bureau of Science to study the various factors affecting the corrosion of galvanized iron and the problem of comparing old and modern galvanized-iron sheets.³

GENERAL CONSIDERATIONS

As is well known,⁴ the durability of galvanized iron under normal service conditions depends on various factors, among them thickness, density, purity, continuity, toughness, and ductility of the coating and the purity of the iron base.

Of the factors mentioned above, thickness of coating is generally considered⁵ the most important. It is true that to some extent zinc will exert a protective influence on iron with which it is in contact, even after the iron is exposed to ordinary corrosive action, but this influence is generally confined to a very limited area. Furthermore the oxidation products of zinc may be electro-negative to iron, so that corrosion would be accelerated instead of retarded. As zinc is removed at a rate depending on the conditions of service to which it is subjected, it is obvious that, other things being equal, the life of a galvanized sheet depends on the amount of zinc per unit area. Actual service tests bear out this view. The actual amount of zinc to be used to give the best service is dependent on economic considerations and on the physical character of the resulting plate. Manufacturers have claimed that a coating heavier than 4.88 grams of zinc per square decimeter (1.6 ounces per square foot) tends to flake off, the result being an imperfect, easily corroded sheet. This claim appears untenable, since the high spelter content of old sheets which have withstood long service exposure has amply

³In recent years galvanized iron with an exceptionally pure iron base has been brought to the Islands. This has not been on the local market long enough to enable us to obtain comparative data concerning its durability under ordinary service conditions.

⁴Cf. Burgess, C. F., *Electrochem. & Met. Ind.* (1905), 3, 17; Walker, W. H., *Proc. Am. Soc. Test. Mater.* (1909), 9, 433.

⁵Walker, loc. cit.

demonstrated that a much heavier coating can successfully be applied.

In hot-galvanizing practice considerable difficulty is encountered in trying to attain high purity of spelter not only because the original spelter may contain such impurities as iron, lead, and other materials which will add impurities to the coating, but also because the iron sheets dipped in the molten bath are slightly dissolved, leading to the formation of zinc-iron alloys on the surface of the iron.

Very few data are available regarding the amounts of impurities permissible in spelter coating.⁶ Cowper-Coles⁷ stated of the impurities in the coating of hot-galvanized iron:

It has been found that iron above 13% makes the zinc too brittle to bend. Lead up to 1% is harmless, but above 1.5% will not dissolve, and the excess collects and forms weak spots.

V. Vegesach,⁸ W. Guertler,⁹ and Arthur and Walker¹⁰ have made elaborate studies of the complex zinc-iron alloys formed during the process of hot galvanizing. Cushman¹¹ has called attention to the fact that the use of zinc chloride or ammonium chloride as flux, sometimes in conjunction with hydrochloric acid, is a strong corrosive mixture and that small portions of the reaction products formed become embodied in the zinc coatings and tend to accelerate corrosion.

Porosity is a defect in zinc coating, since it accelerates the electrolytic corrosion of zinc in contact with iron and thus shortens the life of galvanized sheets under weather exposure. Although "hot galvanized" iron is generally free from pinholes and cracks, "wet galvanized" material, especially when thinly coated, is often extremely porous.¹² Increasing the thickness of the spelter tends to eliminate pinholes and thereby offers less chance for corrosion to start.

Toughness and ductility of coating are important factors, as they determine the resistance of galvanized iron to bending stress and abrasion.

In a well-galvanized sheet the iron base is rarely brought to test under weather exposure until after many years of service.

⁶ Burgess, loc. cit., 17.

⁷ Industries and Iron (1898), quoted by Burgess, loc. cit.

⁸ *Zeitschr. f. anorg. Chem.* (1907), 52, 30.

⁹ *Metallographie* (1911), 353.

¹⁰ *Journ. Ind. & Eng. Chem.* (1912), 4, 398.

¹¹ *Proc. Am. Soc. Test. Mater.* (1909), 9, 129.

¹² Walker, W. H., op. cit., 430.

Spellers¹³ found that the base of galvanized roofing taken from Panama, which had seen service for over twenty-five years and was still in good condition, "proved to be steel, but a larger proportion is wrought iron, and often of inferior quality."

It is apparent that a well-coated sheet with an inferior iron base will last as long as sufficient spelter remains to prevent air and moisture from acting on the iron beneath. It is believed that a pure iron base, per se, does not greatly add to the durability of galvanized sheet in the absence of a liberal amount of coating. The outer layer of the iron base is no longer of original purity, being replaced by a series of iron-zinc alloy layers of different solution tensions. Under the action of weathering this in time offers a field for galvanic action between parts of different electrical potential, until the pure iron base itself is exposed and ultimately becomes corroded. In a corroding solution (Table IV) dezincing pieces from old iron sheets show no greater resistance to corrosion than modern sheets of very pure iron, although the former have given long and satisfactory service.

EXPERIMENTAL PART

The samples used for experimental purposes have been of two kinds: (1) Those that are known to have been under exposure to weather for thirty years and upward and (2) various brands of corrugated sheets recently introduced. The former were taken from roofs in the towns of Batangas and Lipa, representing seacoast and interior highland towns, respectively; the latter were unused specimens of representative brands obtained from the Bureau of Supply or in the open market. The old corrugated sheets were selected from houses whose ages are definitely known. Among the new galvanized sheets are included brands to which belong sheets known to have succumbed to corrosion in from two to five years.

AMOUNT OF SPELTER

Determinations of the quantity of spelter have been made of old corrugated sheets known to have been under weather exposure for more than thirty years. Whenever possible, the unexposed laps as well as exposed portions were analyzed to get a general idea of the amount of spelter originally present. The zinc was determined from pieces 7.62 by 10.16 centimeters (3 inches by 4 inches), these being large enough to give reliable results, yet small enough to enable the detection of marked local irregular-

¹³ *Proc. Am. Soc. Test. Mater.* (1909), 9, 440.

ities. On account of the presence of adhering dirt and films of zinc oxide and carbonate, the zinc was determined directly by precipitation as carbonate, ignition, and weighing as oxide. The results obtained are as follows:

TABLE II.—Amount of zinc on old galvanized sheets.*

[Flat sheet; all 22 gauge.]

Tracing No.	No. of sample.	Year placed under service exposure.	Weight of coating per—	
			Square decimeter.	Square foot.
			Grms.	Ounces.
1	1	1883	7.15	2.34
2	1-X	1883	8.33	2.72
3	2	1882	8.96	2.93
4	2-X	1882	11.02	3.60
5	3	1885	9.71	3.18
6	3-X	1885	9.98	3.26
7	4	1882	8.21	2.68
8	4-X	1882	8.69	2.89
9	5	1885	7.33	2.40
10	5-X	1885	8.42	2.76
11	6	1886	9.07	2.97
12	6-X	1886	12.63	4.13
13	7	1883	7.23	2.36
14	8	1882	8.89	2.91
15	8-X	1882	10.15	3.32
16	9	1884	8.78	2.88
17	b10	-----	9.71	3.18
18	b11	1880	10.47	3.43

* Samples marked X were taken from the unexposed lap of the sheets.

b Old sheets not continuously under service exposure.

For the determination of the weight of coating per unit area on modern, unused sheets, the following procedure was adopted:

Pieces of galvanized sheets cut accurately to 7.62 by 10.16 centimeters (3 by 4 inches) or 5.08 by 5.08 centimeters (2 by 2 inches) are cleaned, washed with alcohol and ether, and are dried and weighed, after which they are immersed in a sulphuric acid solution¹⁴ (containing 3 per cent of the acid by weight) to remove the zinc. The complete solution of zinc is marked by the cessation of hydrogen evolution. By this process the iron base is attacked very little. After the reaction is completed, the iron is brushed, washed, dried, and weighed. The difference between the original weight and the weight after immersion in acid represents the zinc plus a small amount of iron and any

¹⁴ Burgess, loc. cit., recommends 0.66 N, or 3.2 per cent sulphuric acid.

lead or other impurity in the coating. The solution is reduced and titrated with 0.1 *N* potassium permanganate solution to determine the iron dissolved. The amount of iron found is subtracted from the weight of coating dissolved by the acid. The rest may be taken as zinc without appreciable inaccuracy.

Results obtained with new sheets of galvanized iron were as follows:

TABLE III.—*Amount of zinc spelter on modern galvanized sheets.*

[Flat sheet.]

Tracing No.	Sample.		Gauge.	Weight of coating per—	
	Brand.	No.		Square decimeter.	Square foot.
				<i>Grams.</i>	<i>Ounces.</i>
1	A	1	24	5.58	1.83
2	A	2	23	6.38	2.09
3	A	3	23	4.94	1.62
4	A	4	23	4.58	1.50
5	B	1	24	4.73	1.55
6	B	2	23	5.46	1.79
7	B	3	21	4.94	1.62
8	C	1	20	5.83	1.91
9	C	2	24	4.61	1.51
10	C	3	21	4.70	1.54
11	C	4	23	4.88	1.60
12	D	1	25	4.09	1.34
13	D	2	25	3.76	1.27
14	D	3	22	4.34	1.42
15	E	1	23	3.75	1.23
16	E	2	21	4.76	1.56
17	F	1	23	3.60	1.18
18	G	1	22	7.56	2.47
19	G	2	22	6.72	2.20
20	G	3	22	6.56	2.15
21	G	4	22	6.80	2.23
22	H	1	22	3.43	1.12
23	H	2	22	4.27	1.40
24	H	3	22	4.88	1.60
25	I	1	22	6.56	2.15
26	J	1	24	4.48	1.50
27	J	2	26	4.88	1.40

The data in the foregoing tables show that, with two exceptions, even the exposed portions of the old sheets had a heavier coating after thirty years of service than did the modern, unused sheets. The least amount of coating recorded for unexposed portions of old sheets was higher than the greatest determined for the new. The greater amount of zinc on the old as compared with the modern galvanized sheets doubtless

explains to a great extent the marked inferiority of some of the latter. With the exception of brands G, A-2, and I, indicated in Table III, the greater number of samples of modern galvanized iron show less than 6.10 grams of coating per square decimeter (2 ounces per square foot). Sheets of two brands, "B" and "H," are definitely known to have failed in comparatively few years. It has been claimed that brand G gives satisfactory service. As for the rest of the modern brands very little information with regard to their durability is available. Actual weather-exposure tests over long periods of time will be necessary to determine this point, although it is fairly certain that those containing less than 6.10 grams of coating per square decimeter will not withstand the weather for a considerable length of time.

IMPURITIES IN THE COATING

The study of the impurities in the coating was confined to the determination of lead, of the iron alloyed with the zinc, and of the chlorides embodied in the spelter. The alloyed-iron determination presents considerable difficulty in view of the fact that part of the pure iron base is slightly attacked by 3 per cent sulphuric acid and that this attack differs widely with different samples of iron. To determine the extent of the solvent action of the acid, dezincd sheets of 7.62 by 10.16 centimeters (3 by 4 inches) were immersed in fresh standard acid at 30°C. for varying lengths of time. The results obtained are shown in Table IV.

TABLE IV.—*Solvent action of 3 per cent sulphuric acid on iron base.*

[Figures give number of grams per square decimeter.]

Brand.	Weight of sam- ple.	Loss on immersion after—				
		5 min- utes.	10 min- utes.	15 min- utes.	25 min- utes.	35 min- utes.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
A.....	37.0028	0.0328	0.0408	0.0491	0.0973	0.1369
F.....	35.4358	0.0164	0.0216	0.0309	0.0681	0.1276
H.....	38.1037	0.0116	0.0141	0.0302	0.0229	0.0363
G.....	40.4777	0.0093	0.0096	0.0098	0.0119	0.0138
I.....	38.4697	0.0094	0.0089	0.0150		0.0124
S.....	33.1742	0.0111	0.0185	0.0167	0.0486	0.0337

The foregoing table indicates the variation in the solvent action of sulphuric acid which may be expected with different iron bases. In actual determination of the spelter the sheet is not allowed to stay in the acid more than five minutes after all

the zinc has been dissolved, and when that point is reached, the acid solution is considerably weakened, so that the loss of iron is doubtless considerably lower than is indicated by the 5-minute or 10-minute immersion tests. However, the alloyed-iron determination is useful for purposes of comparison and is valuable, even though it may be more or less approximate.

The lead and alloyed iron found in the coating of some of the old and the modern galvanized sheets are shown in Table V.

TABLE V.—*Lead and alloyed iron*^a *in coating of galvanized iron.*

A. ON OLD GALVANIZED SHEETS.

Brand.	Zinc per square decimeter.	Lead in coating.		Iron in coating.	
		Per square decimeter.	Lead, Zinc	Per square decimeter.	Iron, Zinc
	Grams.	Grams.	Per cent.	Grams.	Per cent.
1-X	8.33	0.0701	0.84	0.3081	3.70
2-X	11.02	0.0857	0.78	0.3132	2.84
3-X	9.98	0.0509	0.51	0.3316	3.32
4-X	8.69	0.0406	0.47	0.4623	5.32
5-X	8.42	0.0601	0.71	0.3040	3.61
6-X	12.63	0.0889	0.62	0.4591	3.64
8-X	10.15	0.0893	0.88	0.3375	3.32

B. ON MODERN GALVANIZED SHEETS.

A-2	6.36	0.0171	0.27	0.1982	3.12
A-3	4.91	0.0293	0.59	0.1926	3.92
B-1	4.71	0.0231	0.49	0.2302	4.88
C-1	5.80	0.0340	0.59	0.2293	3.59
C-2	4.58	0.0253	0.55	0.1822	3.98
D-1	4.07	0.0240	0.59	0.1811	4.45
D-3	4.31	0.0253	0.59	0.1475	3.42
E-2	4.74	0.0199	0.42	0.1287	2.72
E-1	3.71	0.0340	0.91	0.2082	5.43
F	3.58	0.0187	0.52	0.3730	10.42
G	7.51	0.0546	0.73	0.1768	2.35
H	3.41	0.0192	0.56	0.1731	5.08
I	6.50	0.0540	0.98	0.2272	3.49

^a Dissolved in 3 per cent sulphuric acid.

Though no great accuracy is claimed for the analytical data on the amounts of iron alloyed with the zinc, they show clearly that the old sheets contained more iron in the coating than did the new; hence the better service of the old sheets cannot be ascribed to greater purity of coating, with respect to alloyed iron.

Although most of the modern galvanized sheets contained

less lead per square decimeter than the old, the lead content, expressed as $\frac{\text{per cent lead}}{\text{per cent zinc}}$, was about the same for both, in no case exceeding 1 per cent. It is scarcely probable that its occurrence in either the new or the old sheets was a very important factor in determining durability. For the majority of the modern galvanized sheets the alloyed iron is considerably less in amount than for the old sheets, averaging about 0.2 gram per square decimeter for the former and about 0.3 gram per square decimeter for the latter. When calculated to $\frac{\text{per cent iron}}{\text{per cent zinc}}$ the greater number of both kinds of sheets give results ranging from 3 to 4 per cent. The maximum for old sheets was 5.32 per cent; the highest among the modern sheets were 10.42 and 5.48 per cent.

Tests for chorides in the sheets analyzed showed the presence of perceptible amounts in all cases, so that no difference in durability could well be ascribed to that cause.

IMPURITIES IN THE BASE

In recent years certain manufacturers have been using iron of exceptional purity, several brands analyzed in this laboratory showing only between 0.20 and 0.40 per cent impurities. So far as length of service of the galvanized sheets under investigation is concerned, the purity of the iron base has been a factor of minor importance and higher impurities than those found in modern sheets have not prevented long service.

PHYSICAL CHARACTERISTICS

With few exceptions, the modern sheets examined have been found to be free from physical defects, thus bearing out the observation made by Walker¹⁵ on hot-galvanized ware in general. They were, on the whole, fairly ductile, free from cracks and pinholes, and showed no marked brittleness. The old galvanized sheets have been found to be slightly less ductile, due to thicker spelter and to oxidation undergone during long years of weather exposure.

CORROSION OF UNUSED SHEETS

Considerable trouble has been experienced in the Philippines with unused sheets of imported galvanized iron which showed advanced stages of corrosion, either upon their arrival in Manila or after short storage periods. In some cases there was

¹⁵ *Proc. Am. Soc. Test. Mater.* (1909), 9, 436.

evidence of wetting by sea water, which, as is well known, is corrosive toward galvanized iron; in some cases sheets showed imperfections in galvanizing, such as pores, ragged edges, and buckles, which are conducive to the formation of centers of corrosion. There were sheets, however, that had imperfections yet which did not show corrosion, and there were cases of accelerated corrosion which imperfections in the coating and insufficiency of spelter did not explain. For example, in one instance galvanized sheets which had arrived apparently in good condition were stacked one over the other without shelter and were thus exposed to sun and rain for about three weeks. The majority of the sheets examined at the end of that time were in an advanced stage of corrosion. Some of the badly attacked sheets were covered by other sheets and were still moist. The average thickness of spelter was 6.41 grams per square decimeter (2.10 ounces per square foot).

There seemed to be but one fact to which the immediate cause of the damage may properly be attributed—that is, the continuous presence of moisture between sheets stacked one upon another, during exposure to weather. This explanation is borne out by the fact that sheets of the same brand that happened to be used for temporary roofs on sheds were in much better condition after nine months' exposure than the damaged sheets of even later arrival.

In a supplementary experiment six pairs of sheets were taken from different brands of the old and modern sheets. The edges were covered with paraffin, and the sheets were placed one on top of the other in pairs. The unexposed sides were kept moist by sprinkling with water once a day. In a few days signs of corrosion were noted and at the end of three weeks all sheets were in an advanced stage of corrosion.

Galvanized sheets undergo accelerated corrosion when the surface is kept moist either by actual wetting with water or by the presence of damp air. It is believed that similar conditions greatly contributed to the corrosion of sheets that arrived in damaged condition or which rusted during storage. The uniformly high temperature and humidity of most parts of the Philippines probably offer exceptionally favorable conditions for corrosion.

PAINT PROTECTION

The frequent failure of modern galvanized sheets in comparatively few years led to the necessity of applying paints, of which red lead, graphite, asphaltum, and oxide of iron are

those most commonly used in the Philippines. A few paint-exposure tests were made, as follows:

A rusted galvanized sheet which had been washed with dilute hydrochloric acid to remove loosely adhering rusts and then washed with water and dried was coated with the following paints:

Primer:		Parts.
Sublimed blue lead		63
Linseed oil		32
Pure turpentine		5
Second coating:		
Bright red oxide of iron		85
Red lead		10
Zinc chromate		5

This paint has been exposed for three years and still renders good protection to the iron sheet. The same paint was applied on a new galvanized sheet, but it peeled off in less than a year.

A graphite paint was applied on a new galvanized sheet. After two years of weather exposure it shows slight peeling off in several parts.

Paint adheres better when it is applied after the surface of the galvanized sheets has undergone considerable oxidation, that is, after a year under weather exposure or when rusts begin to appear. When so applied, it undoubtedly increases the durability of the roofing. The use of paint for modern galvanized roofing is a necessity in the Philippines and will continue to be of immediate consideration to the consumer unless manufacturers put more spelter on their future output.

DISCUSSION OF RESULTS

It is apparent from the foregoing experimental results that the better service given by the old galvanized iron as compared with the modern product imported to the Philippines is accounted for by the greater amount of coating on the former. This conclusion is in accord with observations made by others elsewhere. For example, Van Gundy¹⁶ noted that galvanized plate which had seen service of twenty or twenty-five years in Panama was better than plate which had been in service less than two years. Referring to the old galvanized sheet he said:

Yet, even after this service, I found that it had three times as much zinc on it as the American manufacturers put on their plate, even the best in the market.

¹⁶ *Proc. Am. Soc. Test. Mater.* (1909), 9, 41.

Walker¹⁷ found that a galvanized-wire fence carrying 3.9 per cent of zinc was still in good condition after four years of service, while another sample which carried 1.4 per cent was badly rusted in three years. He makes the following observations:

In every instance where a very durable fence was found, the coating of zinc was relatively very thick; while on the other hand, the fences which showed marked corrosion in from one to two years proved to have almost no zinc on the iron, the zinc color being due to a layer of alloy alone.

In accordance with the conclusions of other observers, and from the results obtained, it is evident that in the manufacture of galvanized sheets the application of the "maximum amount of zinc consistent with the practical possibility of its manufacture"¹⁸ should be striven for, if sheets are expected to render long service on exposure. Economic and physical considerations should be the limiting factors in deciding the minimum amount of spelter per unit area. In recent years the tendency among manufacturers to diminish the thickness of the spelter no doubt has had an important bearing on the durability of modern corrugated sheets.

Various standards of thickness of coating have been used, among them the following:

TABLE VI.—*Various standards of coating.*

Source.	Per square decimeter (flat).	Per square foot (flat).
	<i>Grams.</i>	<i>Ounces.</i>
Kidder, 1913 edition, p. 1439	7.63	2.50
American Civil Engineer's Pocket Book, 1913 edition, p. 393	16.58	5.44
Standard Specifications of the Isthmian Canal Commission for 1909	7.63	2.50
Trautwine, 1909 edition, p. 881	4.88	1.60
Altoona car roofing, <i>Proc. Am. Soc. Test. Mater.</i> (1909), 9, 441	12.21	4.00

The present work indicates that, for the Philippines at any rate, 7.63 grams per square decimeter (2.50 ounces per square foot) of spelter is the minimum coating for galvanized sheets which will ensure satisfactory service.

None of the other factors studied would account for the differences in durability noted between old and new galvanized iron. All sheets tested showed the presence of chlorides. The lead found in the old and modern sheets is approximately the

¹⁷ Ibid. (1909), 9, 43.

¹⁸ Cushman, *ibid.* (1909), 9, 143.

same when calculated on the basis of spelter content, and probably in no case was it high enough to affect durability adversely. The iron dissolved by 3 per cent sulphuric acid assumed to represent the iron alloyed with zinc is approximately the same in the old and modern sheets when calculated on the basis of spelter content. Modern sheets are not inferior with respect to continuity and ductility of coating as compared with the old sheets. The iron body of modern galvanized sheets is of high purity and is equal or superior in quality to that of old sheets.

SUMMARY

The importation of galvanized-iron roofing to the Philippines approximates 1,500,000 pesos in value annually. Many of the recently imported brands fail rapidly, while certain brands have given satisfactory service for over thirty years.

Of the various factors influencing the durability of galvanized iron which have been studied with a view toward accounting for the difference in behavior of old and modern sheets, it appears evident that the greater weight of zinc per unit area on the former accounts for the greater durability. The modern sheets were not inferior to the old product with respect to the presence of impurities in the coating or in the iron base or with respect to continuity, ductility, or toughness of coating.

For satisfactory service in the Philippines, galvanized iron should have a coating of not less than 7.63 grams per square decimeter (2.50 ounces per square foot).

The advanced corrosion often noted in the Philippines of sheets newly arrived or kept in storage probably finds explanation in the fact that galvanized iron corrodes very rapidly when continually kept moist either by actual contact with water or by the presence of damp air.

Proper paints, applied after the surface of sheets has become well roughened by exposure, will greatly increase the life of modern galvanized iron.

THE DETINNING AND ANALYSIS OF TIN PLATE ¹

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INTRODUCTION

Practically all the tin plate on the market is made by a hot-dip process—by immersing carefully cleaned sheet iron in a bath of molten tin. The coating formed by this process varies from almost pure tin at the outer surface of the plate to a tin-iron alloy rich in iron near the surface of the iron base. Often varying amounts of lead are used in the molten bath.

The removal of the coating from tin plate, both for the commercial recovery of tin and for analytical purposes, has been the subject of much study. Among the commercial methods the most important are the electrolytic detinning in alkaline solution,² the chlorine process,³ and various modifications of these.⁴

In addition, a large variety of methods have been proposed, such as the mechanical separation of tin from tin plate by agitation of a mass of tin scrap with liquid air;⁵ the treatment of the material with superheated steam,⁶ whereby tin is fused and loosened by the formation of iron oxides; solution of tin in strong commercial hydrochloric acid, kept cold⁷ to prevent the solution of iron; removal of tin by a solution of sodium plumbate;⁸ or electrolysis in a bath of phosphoric acid.⁹

Many processes¹⁰ have been recommended for the removal and determination of tin and lead in tin plate, among

¹ Received for publication July 17, 1916.

² Keith, U. S. Patent 176,658 (1876).

³ Cf. *Electrochem. & Met. Ind.* (1909), 7, 79.

⁴ Skinner, R. P., German detinning methods, *Det. Ind.* (1914), 12, 236. Detinning industry, *Electrochem. & Met. Ind.* (1909), 7, 79.

⁵ Phelps, W. J., U. S. Patent 952,351 (March, 1910).

⁶ Wiltreck, H. C., German Patent 261,522 (February, 1912).

⁷ Calmels, J. M., French Patent 448,004 (September, 1902).

⁸ Ramage, A. S., *Met. & Chem. Eng.* (1911), 9, 219.

⁹ Battle, A. E., Brit. Patent 14,514 (June, 1914).

¹⁰ Cf. Serger, H., *Zeitschr. f. d. Untersuch. d. Nahrungs- u. Genussm.* (1913), 25, 465.

them the mechanical removal¹¹ of the tin after heating over a Bunsen flame; the digestion at boiling temperature with sodium peroxide,¹² the difference in weight before and after treatment serving as an indication of the amount of coating; the solution of the tin coating in 12.5 per cent hydrochloric acid¹³ and subsequent precipitation of the tin as sulphide, heating, and final weighing as oxide; the solution in 10 per cent hydrochloric acid,¹⁴ precipitation with ammonium sulphide, and heating, after certain precautions, with ammonium carbonate; and the heating of tin plate with dry sodium peroxide,¹⁵ solution of the melt in water, acidifying with sulphuric acid, washing, heating, and weighing the precipitated oxide. I. H. Aupperle¹⁶ suggests (1) the solution of the tin in hydrochloric acid, with certain precautions, and the final determination of tin by titration with iodine solution, or (2) the removal of tin with concentrated sulphuric acid and the determination of the iron in the solution, the tin being obtained either by difference or by direct analysis as above.

The above methods either give merely the amount of tin present or else the total amount of plate (tin, lead, and iron alloy in the coating). If the amounts of tin and lead are desired, additional processes are required.

Directions for a simple method for the determination of lead, as given by Serger,¹⁷ are as follows:

Take 0.1 gram iron-free tin, carefully scraped from heated tin plate, decompose with 3 cubic centimeters of concentrated nitric acid on a steam bath, and evaporate to dryness three times. Add 10 cubic centimeters of water, allow to stand on a water bath for ten minutes, filter into a 100 cubic centimeter flask, and dilute to the mark with distilled water. Shake well, use 10 cubic centimeters in a large test tube, and add 10 cubic centimeters of fresh hydrogen sulphide water. Compare the color obtained with a standard made by adding 2, 5, 10, and 20 drops of a water solution, containing 0.16 gram of lead nitrate per 100 cubic centimeters (1 cubic centimeter=0.001 gram metallic lead) to 10 cubic centimeters of water and 10 cubic centimeters hydrogen sulphide water.

¹¹ Serger, loc. cit.

¹² Meyer, K., *Zeitschr. f. angew. Chem.* (1909), 22, 68.

¹³ Serger, loc. cit.

¹⁴ Mastbaum, H., *Zeitschr. f. angew. Chem.* (1897), 10, 329.

¹⁵ Angenot, H., *ibid.* (1904), 17, 521.

¹⁶ *Metal. Ind.* (1914), 12, 327-328.

¹⁷ Loc. cit.

For rapid, practical tests, where many examinations must be made to determine the quality of a large shipment of tin plate, simple determinations of the amount of coating per unit area will doubtless be found sufficient in addition to tests on uniformity of coating. Many of the procedures outlined are unnecessarily tedious.

In most of the foregoing methods the amount of iron alloyed with the tin is not determined, although it appears obvious that it is a factor having an important bearing on the quality of the resulting tin plate. A method which will first remove the coating, including the tin-iron alloys, from tin plate and which will enable the subsequent determinations of at least the tin and iron in the coating ought to yield more valuable information concerning the quality of tin plate than a determination of the tin only or of the tin and lead in the coating.

The work here recorded was done for the purpose of studying and developing methods of removing tin from plated iron without attack on the iron base, with special references to the analysis of tin plate.

EXPERIMENTAL PART

Different brands of tin plate were used in the work here recorded, but none of these contained lead. A sample of tin plate of uniform appearance and apparently good quality was cut into squares 5 centimeters on a side, cleaned with alcohol and ether, and analyzed according to the method of Aupperle,¹⁸ the final titration for tin being made with iodine solution. The results with different squares were as follows:

TABLE I.—Analysis of tin plate by Aupperle method (titration with iodine solution).

No.	Weight of sample. ^a	Weight of tin.	Weight per unit area.		Tin in tin plate.
			Per square decimeter.	Per square foot.	
	Grams.	Grams.	Grams.	Ounces.	Per cent.
1	4.340	0.064	0.256	0.084	1.48
2	4.340	0.072	0.288	0.094	1.66
3	4.293	0.068	0.272	0.089	1.58
4	4.330	0.071	0.284	0.093	1.64
5	4.354	0.064	0.256	0.084	1.47
Average	4.331	0.068	0.271	0.089	1.57

^a Size of plate, 5 by 5 centimeters.

¹⁸ Loc. cit.

When stripped by immersion in boiling sodium peroxide solution ¹⁹ samples of the same tin gave the following results:

TABLE II.—*Analysis of tin plate by the Meyer method.*

No.	Weight of sample. ^a	Loss after treatment.		Coating per unit area.	
				Per square decimeter.	Per square foot.
	Grams.	Grams.	Per cent.	Grams.	Ounces.
6	4.346	0.082	1.89	0.328	0.107
7	4.360	0.085	1.95	0.340	0.111
8	4.289	0.078	1.82	0.312	0.102
9	4.310	0.075	1.74	0.300	0.098
Average	4.326	0.080	1.85	0.320	0.1045

^a Size of samples, 5 by 5 centimeters.

The Meyer method gives concordant and reliable results, but it is clumsy, because of the unavoidable and disagreeable spattering attendant on the use of sodium peroxide, and because long and repeated treatment is necessary to ensure complete removal of the coating.

The results obtained by this method are higher than those obtained by direct analysis of tin, the difference (about 0.05 gram) representing the amount of iron removed with the tin plate. That this iron is actually part of the alloy and is not due to attack on the base is shown by the fact that there was no further loss in weight on subsequent treatment with sodium peroxide.

Since iron is an insoluble anode in certain alkaline and oxidizing solutions, other metals can readily be stripped from it electrolytically.²⁰ For the work here recorded a 30 per cent solution of sodium nitrate was employed as stripping bath, and the plate was made the anode. As will be seen, the results obtained are comparable with those obtained with sodium peroxide. Comparable results were obtained with sodium or potassium hydroxide solutions, but with these the action was so slow that their use is not recommended.

¹⁹ Meyer, op. cit.

²⁰ Cf. Burgess, C. F., *Trans. Am. Electrochem. Soc.* (1903), 4, 31.

TABLE III.—Analysis of tin plate by electrolysis.*

A. IN A 30 PER CENT SODIUM NITRATE SOLUTION.

No.	Weight of sample. ^b	Loss after treatment.		Coating per unit area.	
				Per square decimeter.	Per square foot.
	Grams.	Grams.	Per cent.	Grams.	Ounces.
10	4.346	0.082	1.88	0.328	0.108
11	4.281	0.080	1.87	0.320	0.105
12	4.261	0.079	1.85	0.316	0.104
13	4.296	0.080	1.84	0.320	0.105
Average	4.296	0.080	1.86	0.321	0.105

B. IN A 20 PER CENT SODIUM HYDROXIDE SOLUTION.

14	4.337	0.072	1.66	0.288	0.094
15	4.292	0.078	1.84	0.302	0.102

* Voltage, 3.5; amperage, 0.7; time, about ten minutes.

^b Size of samples, 5 by 5 centimeters.

This procedure offers an extremely simple and rapid method of analysis. Stripping is accomplished in a few minutes. There is no danger of attacking the iron of the base. The iron of the alloy removed from the plate is left in the bath in such form that it can be readily recovered as ferric hydroxide and can be determined quantitatively.

By reference to the results obtained in Table II it is evident that the two methods are strictly comparable.

In a study of the stripping of galvanized iron, we called attention ²¹ to a number of salts which would be replaced in solution of metals by zinc but not by iron. As zinc is generally electropositive to iron in aqueous baths, metals intermediate in the potential series to zinc and iron should form salts which strip zinc from iron. Such salts were readily found, among them a number which might have been expected to attack iron as well as zinc. To find salts which will strip tin from iron is more difficult, since tin is electronegative to iron in many aqueous solutions, and salts which dissolve the former might naturally be supposed to attack the latter.

²¹ *This Journal*, Sec. A (1916), 11, 144.

Basic lead acetate solution will strip zinc from iron,²² but leaves tin plate unattacked. Lead acetate does not affect tin plate either in neutral or (acetic) acid solution, but lead acetate or other lead salts, in solutions made alkaline with sodium or potassium hydroxide, strip tin from plated iron very rapidly, depositing lead in a spongy, easily removed condition. The accuracy of the method may be judged by the tests made on samples of the same tin plate previously analyzed.

TABLE IV.—*Analysis of tin plate by immersion in alkaline lead acetate (sodium plumbite) solution.*

FIVE-MINUTE TEST.

No.	Weight of sample.*	Loss after treatment.		Coating per unit area.	
				Per square decimeter.	Per square foot.
	Grams.	Grams.	Per cent.	Grams.	Ounces.
16	4.285	0.078	1.82	0.312	0.102
17	4.214	0.076	1.80	0.304	0.100
18	4.221	0.072	1.70	0.288	0.094
19	4.325	0.073	1.69	0.292	0.096
Average	4.261	0.075	1.75	0.299	0.098

THREE-DAY TEST.

16	4.285	0.082	1.91	0.328	0.107
17	4.214	0.082	1.95	0.328	0.107
18	4.221	0.077	1.85	0.308	0.101
19	4.325				
Average	4.261	0.080	1.90	0.321	0.105

* Size of samples, 5 by 5 centimeters.

These data are again comparable with those obtained by the methods previously outlined. Concordant results are obtained, and unless great refinement is desired, the method is sufficiently rapid and accurate to serve as a reliable guide in the judgment of tin plate. Compared with the data previously recorded, the results obtained with alkaline lead acetate solution are a trifle low, showing that all of the tin-iron alloy is not removed immediately by this method. As a matter of fact, the lead solution does strip nearly all of the iron-tin alloy from the iron if the time of immersion is prolonged, the reaction being practically

²² Patrick, W. A., and Walker, W. H., *Journ. Ind. & Eng. Chem.* (1911), 3, 239.

completed after an hour or two. Doubtless the presence of much lead in a tin coating would lessen the accuracy and applicability of this method.

Other salts of lead yield similar results, but the reaction is by no means confined to lead salts. Aluminium nitrate, made alkaline with sodium hydroxide, will strip tin, although the action is extremely slow. A solution of copper sulphate and tartaric acid, made alkaline with sodium hydroxide, has a similar effect. Chromium nitrate solution attacks both tin and iron, but the same solution with enough sodium hydroxide added to make a clear liquid will dissolve only the tin. The data secured with typical solutions are given herewith, the tables showing the results obtained with two different samples of tin plate. Lead salts are the only ones listed to be recommended for analytical work.

TABLE V.—*Detinning by immersion.*

PLATE A.^a

No.	Solution used.	Weight of sample.	Loss on immersion.		Weight of coating.	
					Per square decimeter.	Per square foot.
		Grams.	Grams.	Per cent.	Grams.	Ounces.
16-19	Lead acetate and sodium hydroxide.....	4.261	0.075	1.76	0.300	0.098
20	Lead chromate and sodium hydroxide.....	4.351	0.071	1.63	0.284	0.093
21	Chromium nitrate and sodium hydroxide.....	4.401	0.067	1.61	0.268	0.088
22	Aluminium nitrate and sodium hydroxide.....	4.321	0.065	1.52	0.260	0.085
23	Copper sulphate, tartaric acid, and sodium hydroxide.....	b1.224	0.022	1.79	0.303	0.099
24	Nitric acid, concentrated.....	4.272	0.069	1.61	0.276	0.090
25do.....	4.299	0.066	1.54	0.264	0.086

PLATE B.^c

26	Lead acetate and sodium hydroxide ...	5.202	0.064	1.23	0.248	0.081
27do.....	5.314	0.066	1.24	0.256	0.084
28	Lead nitrate and sodium hydroxide ...	5.341	0.066	1.24	0.256	0.084
29do.....	5.420	0.071	1.31	0.275	0.090
30	Lead chromate and sodium hydroxide..	5.526	0.063	1.14	0.244	0.080
31do.....	5.452	0.065	1.19	0.252	0.083
32	Aluminium nitrate and sodium hydroxide.....	5.374	0.071	1.32	0.275	0.090

^a Size of samples, 5 by 5 centimeters, except as noted.

^b Size of sample, 1.45 by 5 centimeters.

^c Size of samples, 2 by 2 inches (5.08 by 5.08 centimeters).

Concentrated nitric acid will remove tin without attack on the iron base, although it will entirely destroy a piece of galvanized iron. Both tin and zinc are anodic to iron in concentrated nitric acid, and zinc is anodic to tin.

The experiments in the preceding tables are of interest, not only because of the apparent "reversals" of potential of tin, but also because of the fact that many of the reactions recorded took place in alkaline solutions in which the metals used (chromium, aluminium, lead, etc.) are generally thought to be part of the acid radicals.

AMOUNT OF IRON IN THE COATING

The amount of iron alloyed with tin depends on the temperature and purity of the plating bath and doubtless varies with different brands of tin plate. It is reasonable to suppose that it should be an important factor in determining the quality of tin plate and its resistance to corrosion. The various brands analyzed by us showed iron contents in the tin coating of about 0.05 gram per square decimeter.

SIZE OF SAMPLES TO BE USED FOR ANALYSIS

The analytical data previously recorded indicate the lack of uniformity of coating to be expected in commercial tin plate. Although errors are undoubtedly caused by failure to cut samples of tin plate accurately to squares of the required size, it is apparent that great discrepancies in uniformity of coating exist, even in samples cut from the same sheet. Obviously more concordant results would be obtained if larger samples were used, but in that case the analyst might easily fail to detect local defects in the coating. With the methods outlined, squares 5 by 5 centimeters, or at most 5 by 10 centimeters, should be ample for analytical purposes and should yield more reliable data than larger samples.

STANDARDS FOR TIN PLATE

The quality of a galvanized iron is determined chiefly by the thickness of the coating, since zinc, under ordinary service conditions, itself corrodes and inhibits the corrosion of iron even after the latter is exposed. Tin, on the other hand, frequently accelerates the corrosion of iron; its protective influence is mechanical. Uniformity of coating is, therefore, an essential requirement for good tin plate, and a test, such as the one devised by W. H. Walker,²³ for the detection of pinholes and

²³ *Journ. Ind. & Eng. Chem.* (1909), 1, 440.

other inequalities in tin plate is of great importance in determining quality. Leaving out of consideration the question of the purity of tin plate, it is evident that specifications should require certain standards, both for thickness and for uniformity of coating.

Obviously the amount of coating necessary for good tin plate will depend, to a large extent, on the service to which it is subjected. The specifications for the United States Navy Department²⁴ call for 5 pounds of tin per 112 sheets 14 by 20 inches in size, corresponding to a coating of 1.123 grams per square decimeter (0.367 ounce per square foot). According to Serger,²⁵ a coating of 0.3 gram of tin per square decimeter of tin plate (that is, 0.15 gram per square decimeter of surface) is sufficient to make plate resistant to the corrosive influences to which canned goods are subjected, and no material which had given satisfactory service showed a smaller amount of tin. The few data at hand in the Bureau of Science tend to confirm the conclusion of Serger and indicate that the figures given by him represent the lower limit for good tin plate. For example, a certain shipment of tin cans corroded so badly during an eighty-day voyage from the United States to Manila that a large amount of the contents leaked out. The corrosion was entirely from the outside, the interior of the cans remaining bright and unspotted. There was no evidence of sea-water damage or undue corrosive influence. Upon analysis the cans were found to have a coating of 0.245 to 0.250 gram of tin per square decimeter.

SUMMARY

A number of methods of stripping tin plate without attack on the iron base have been studied. Of these, detinning by means of an electric current, making the plate the anode in a bath of sodium nitrate, and stripping by immersion in a solution of a lead salt made alkaline with sodium hydroxide (sodium plumbite) can be recommended for rapid and accurate analytical work.

²⁴ No. 47 T 1 (February 15, 1912).

²⁵ Loc. cit.

REVIEW

Practical | Physiological Chemistry | [3 lines] | by | Philip B. Hawk, M. S.,
Ph. D. | [2 lines] | fifth edition, revised and enlarged | [4 lines] |
Philadelphia | P. Blakiston's Son & Co. | 1012 Walnut Street | 1916 |
Cloth, pp. i-xiv+1-638.

The great advances in physiological chemistry are very well illustrated by the numerous editions of books dealing with this phase of chemistry put out in their attempts to keep abreast of the subject.

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This last edition has been brought up-to-date by thoroughly revising and rewriting the preceding edition and by adding five new chapters. These chapters are: Chapter III on Nucleic Acids and Nucleoproteins, Chapter VIII on Gastric Analysis, Chapter XI on Intestinal Digestion, Chapter XVI on Blood Analysis, and Chapter XXVII on Metabolism. The system of including laboratory directions in the text and the use of black-faced type for the most important and reliable of these tests and methods are valuable features of this book. An examination of this latest edition impresses one with the important part given to the discussion of the function of enzymic activity in the everyday life of the human being.

The book is printed on good paper, is attractively and well bound, and is well printed. A number of errors have escaped the notice of the proof reader, as, *creatinine* has been used for *creatine* (page 508).

The book is excellent in subject matter and arrangement and is a valuable contribution to this phase of chemical literature, due to Doctor Hawk's wide experience and extensive knowledge of the subject.

H. C. B.

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